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Chemicals in the Community:

Implementing Regional Air Monitoring Programs

Prepared for the

Chemical Manufacturers Association

By

NUS Corporation

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Other Related Documents

CMA, as part of its ongoing technical education and communication efforts, developed this document as part of its "Chemicals in the Community:" series. Other documents in this and related series include:

CHEMICALS IN THE COMMUNITY Series includes:

Methods to Evaluate Airborne Chemical Levels, May 1988.
A resource document presents two general approaches for placing emission levels in context: data-base driven and model driven. Using these two approaches, 8 methods, are described to evaluate the health impact of airborne releases.

Member price $8.00; Non-member price $12.00.

Implementing Regional Air Monitoring Programs, February 1990.
A manual to assist companies establish regional air monitoring programs. This document covers both the policy issues and the technical details of setting up a regional air monitoring project.

Member price $20.00; Non-member price $40.00.

Understanding Environmental Fate, in preparation.

IMPROVING AIR QUALITY Series includes:

Guidance for Estimating Fugitive Emissions from Equipment, January 1989.
A guidance manual of fugitive emission testing for plants that want to conduct accurate leak rate estimations. This manual includes the EPA protocol with notations for implementation by the chemical industry.

Member price $20.00; Non-member price $30.00.

Fugitive Emission Workshop Videotapes
These videotapes cover some of the topics plant personnel ask about when setting up a testing program for equipment leak, detection, and repair (LDAR).

	Minutes	Member Price	Non-Member Price
Tape I: Overview	42	$ 75.00	$112.50
Tape II: Screening	58	75.00	112.50
Tape III: Bagging	38	75.00	112.50
All Three Tapes		225.00	337.50

All tapes are available in ½ and ¾ inch formats.

POSSEE Software (Plant Organizational Software System for Emissions from Equipment)
POSSEE is a software data entry system for fugitive emissions testing designed exclusively for CMA. POSSEE can help you set up a testing program, enter data, and develop estimates of the fugitive emissions at your plant.

Member price $150.00; Non-member price $225.00.

A Guide to Estimate Secondary Emissions, In Publication.
A guidance manual for estimation emissions from secondary air sources for SARA 313 reporting.

Member price $40.00; Non-member price $60.00.

PAVE Software, In Development.

To order these documents, please refer to order form on the last page of this publication.

Executive Summary

As responsible members of the communities in which they operate, industries are increasingly motivated to participate in efforts to measure concentrations of chemicals in the community.

Publics (e.g., community, concerned citizens' groups, business, and Federal, state, and local regulatory agencies) have become very aware of the presence of chemicals in the air. These audiences are rightfully demanding credible information about levels, sources, and effects of chemicals to which they may be exposed. They are expecting information to:

- Determine ambient concentrations of airborne pollutants, commonly known as "air toxics."
- Fill data gaps regarding concentrations of airborne pollutants in the community.
- Respond to local, state, or Federal regulatory requirements.
- Provide data to evaluate the impacts of airborne chemicals.
- Identify contributors of toxic air pollutants in the community. Contributors can include mobile sources, commercial and residential chemical users, and industrial chemical processes. In addition, long-range transport of air pollutants may contribute chemicals to the community.

Toxic air pollutant monitoring may be needed as part of ozone precursor studies, emergency release evaluations, and source-receptor relationship studies, including model validations.

Regional monitoring programs benefit both the community and industry participants. These programs provide unique opportunities for cooperative efforts involving industry, regulators, and the community. Ambient data collected can be of great value to all parties. These data provide a technically sound basis for regulatory decision-making and public policy formation.

The purpose of this document is to provide information to those individuals responsible for deciding if and how an air toxics monitoring program should be undertaken. This document is directed to industry representatives who are interested in monitoring levels of toxic air pollutants in regions where they operate. It provides a framework for organizing and participating in regional air monitoring programs. This guidance allows flexibility in tailoring the program to meet specific local needs. It also emphasizes the cooperative nature of such projects and the steps needed to involve the public and regulators during the program planning process.

The document also provides specific technical recommendations for conducting an air toxics survey followed by longer term regional air monitoring. These recommendations are:

- Perform air toxics survey monitoring study for preliminary determination of community concentrations as follows:
  - Program duration should be 30 to 90 days.
  - Samples are to be collected for 3 to 24 hours every other day or once in 3 days, depending on the study's specific objectives.
  - The number of monitoring stations established depends on specific local conditions and program objectives. A minimum of two monitoring stations should be implemented in this type of study.
  - A portable meteorological station should be used.

- Perform regional air toxic monitoring to establish regional community concentrations as follows:
  - Program duration should be one year or more.
  - Samples are to be collected for 24 hours every sixth day or less.
  - The number of monitoring stations established depends on specific local conditions. For flat or gently rolling topography with no land/water interface, the network should contain a minimum of three monitoring stations, with one station representing prevailing upwind conditions and the others representing prevailing downwind stations. The number of monitoring stations can be re-evaluated after one year of operation.
  - The number of meteorological stations established depends on local specific conditions such as topography, the distance between individual monitoring stations, and program objectives. In general, a meteorological station should be located next to each air sampling station. However, this recommendation could be modified, depending on local specific conditions.
- Use the SUMMA passivated canister for sampling of volatile organic compounds (VOCs) and gas chromatography/mass spectrometry (GC/MS) for subsequent analysis.

Estimated costs for setting up and operating a monitoring network are included in this document. For example, the estimated first-year cost for installing and operating a regional air toxics monitoring network consisting of four canister samplers each operating every sixth day at three sites, plus one meteorological station, ranges between $300,000 and $400,000. Procurement and start-up costs comprise about 25 percent of these costs, with the remainder allocated to operation, analysis, and data management expenses.

The emphasis of a regional air monitoring program must be on quality to ensure credibility. The quality of the program depends directly on quality management and quality contractors. The data collected during the program must be impeccable to withstand peer review. It is important that other industries, government agencies, and the public be involved to gain credibility for the program.

1.0 INTRODUCTION

Before starting a monitoring project, industry must establish a clear understanding of the overall goal, objectives, and driving forces behind ambient air toxics monitoring. This includes identifying community concern and regulatory requirements.

This document has been developed for the Chemical Manufacturers Association (CMA) by NUS Corporation. Its ultimate objective is to guide planning and implementation of regional air toxics monitoring programs. The specific objectives of this document are:

- To provide a basic, yet comprehensive, guide for planning and implementing regional air toxics monitoring programs.
- To allow flexibility in tailoring regional programs to meet specific local needs.
- To provide a framework that will ensure consistency between the various regional programs, which will allow the development of a useful data base.
- To provide a systematic process for the decision maker (usually the facility or plant manager within a region) to ensure the development and implementation of successful regional air toxics monitoring programs.

Those interested in monitoring air toxics levels in communities where they operate will find this document useful. It primarily addresses how to plan and operate regional monitoring networks for volatile organic compounds (VOCs). However, monitoring for other constituents, such as metal particulates, are covered in a more condensed manner.

The document includes specific recommendations for establishing a regional air toxics monitoring network. These recommendations can be modified as needed from one region to another. Those industries interested in establishing monitoring networks should consider a joint program with regulators and the public. These networks can provide technically sound information to participating sponsors, the public, and regulatory and planning agencies.

The document provides guidance in the following areas:

- Involving regulators, the public, and other interested parties.
- Structuring the management of a regional air toxics program.
- Developing a monitoring program plan.
- Implementing sampling and analysis activities.
- Ensuring the quality of collected data.
- Organizing and reporting monitoring results.
- Estimating costs of monitoring programs.

1.1 ORGANIZATION OF THE DOCUMENT

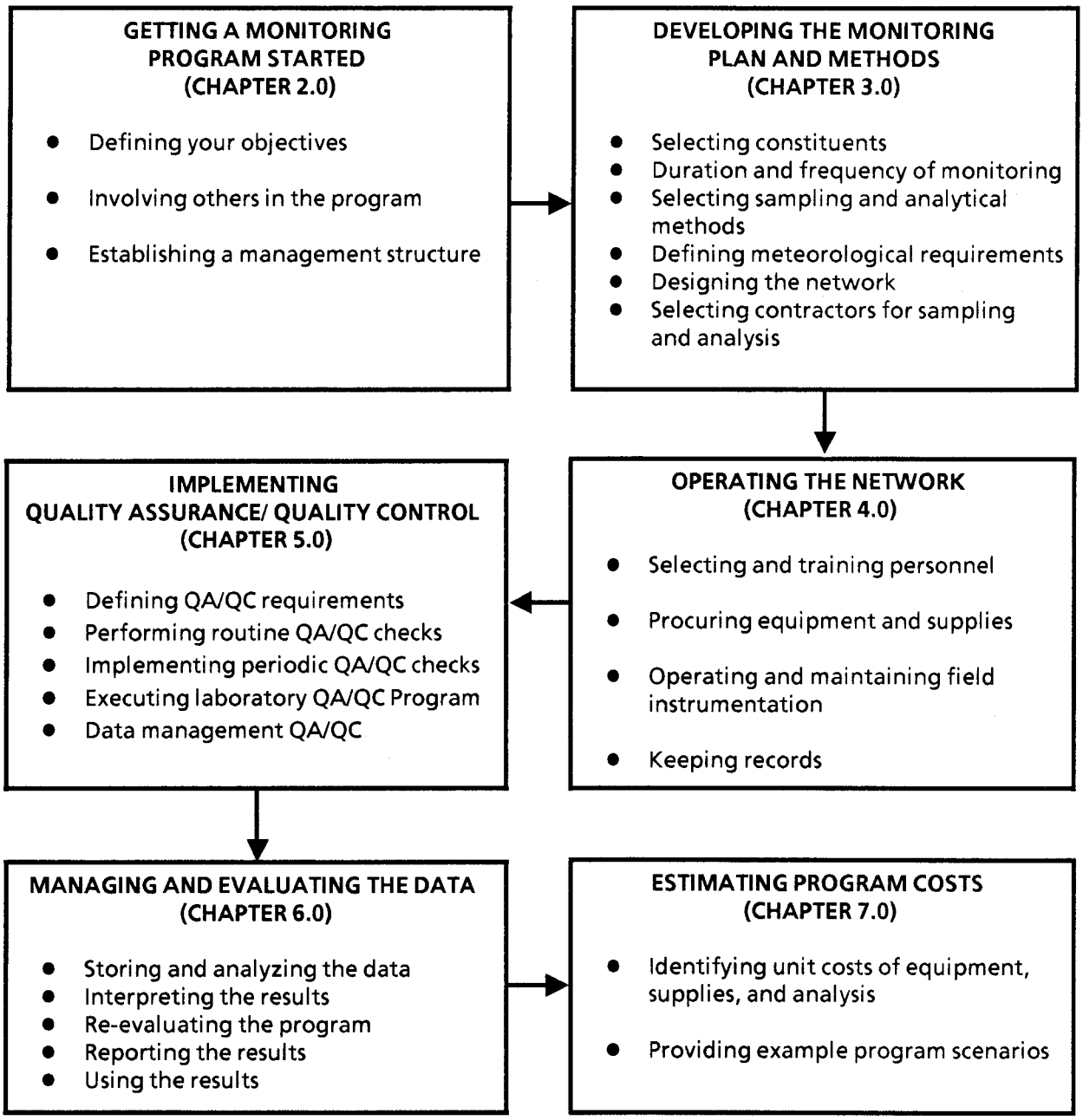
This document is intended to be both a management- and technical-level planning tool which can be useful as a guide for directing CMA member staff and contractor activities in regional air toxics monitoring programs.

Program elements associated with the planning and implementation of regional ambient air toxics monitoring are shown in Figure 1-1. This figure includes six key elements. Each represents a chapter in this document and is summarized as follows:

- Chapter 2.0 (Getting a Monitoring Program Started) discusses the motivation and philosophy behind such programs; who should be involved in the program (public, regulatory agencies, other industries) and why; and what management factors should be considered in designing and implementing a regional air toxics monitoring program.
- Chapter 3.0 (Developing the Monitoring Plan and Methodologies) describes the process for developing monitoring program plans. Key features include selecting constituents to be monitored; selecting program duration and frequency; selecting sampling and analytical methods; defining meteorological program requirements; designing elements of the network; and selecting contractors for sampling and analysis.
- Chapter 4.0 (Operating the Network) describes the process for selecting and training personnel; procuring equipment; operating and maintaining field instrumentation; and keeping records.
- Chapter 5.0 (Implementing Quality Assurance/ Quality Control) provides guidance for routine and periodic field, laboratory, and data management QA/QC requirements.
- Chapter 6.0 (Managing and Evaluating the Data) describes the process of storing, reducing, processing, validating, analyzing, interpreting, reporting, and using data.
- Chapter 7.0 (Estimating Program Costs) provides estimates for unit costs of equipment and laboratory analysis as well as estimates of capital and operating costs, for example, program scenarios.

FIGURE 1-1

ELEMENTS TO PLAN AND IMPLEMENT A REGIONAL AIR TOXICS MONITORING PROGRAM


GETTING A MONITORING PROGRAM STARTED (CHAPTER 2.0)
• Defining your objectives
• Involving others in the program
• Establishing a management structure
DEVELOPING THE MONITORING PLAN AND METHODS (CHAPTER 3.0)
• Selecting constituents
• Duration and frequency of monitoring
• Selecting sampling and analytical methods
• Defining meteorological requirements
• Designing the network
• Selecting contractors for sampling and analysis
IMPLEMENTING QUALITY ASSURANCE/ QUALITY CONTROL (CHAPTER 5.0)
• Defining QA/QC requirements
• Performing routine QA/QC checks
• Implementing periodic QA/QC checks
• Executing laboratory QA/QC Program
• Data management QA/QC
OPERATING THE NETWORK (CHAPTER 4.0)
• Selecting and training personnel
• Procuring equipment and supplies
• Operating and maintaining field instrumentation
• Keeping records
MANAGING AND EVALUATING THE DATA (CHAPTER 6.0)
• Storing and analyzing the data
• Interpreting the results
• Re-evaluating the program
• Reporting the results
• Using the results
ESTIMATING PROGRAM COSTS (CHAPTER 7.0)
• Identifying unit costs of equipment, supplies, and analysis
• Providing example program scenarios

1.2 WHY CONDUCT AN AIR TOXICS MONITORING PROGRAM

Several reasons drive the need for regional air toxics monitoring programs. They include corporate positions, regulatory requirements, and public concerns. Communities have become very aware of the presence of chemicals in the air and are demanding credible information about the levels, sources, and effects of chemicals to which they may be exposed. Industry is increasingly motivated to:

- Determine ambient concentrations of airborne pollutants, commonly known as "air toxics."
- Fill data gaps regarding concentrations of airborne pollutants in the community.
- Respond to local, state, or Federal regulatory requirements.
- Provide data to evaluate the impacts of airborne chemicals.
- Identify contributors of toxic air pollutants in the community. Contributors can include mobile sources, commercial chemical and residential chemical users, and industrial chemical processes and long-range transport of air pollutants.

Public awareness of toxic chemical emissions from industrial and other sources and their effects on public health and the environment has increased since the enactment of the Right-to-Know Act under the 1986 Superfund Amendments and Reauthorization Act (SARA). Federal, state, and local jurisdictions have enacted regulations or policies that require consideration of air emissions when issuing permits for both new and existing sources.

Regional air monitoring programs can provide information about air quality. These data can address public and industry concerns and can provide a better understanding of the impact of air toxics emissions. This knowledge is of particular importance in regions with large industrial complexes.

Results of well-designed and implemented air monitoring programs provide a "ground truth" for what is happening in the area or region of interest. In this respect, such programs can be viewed as proactive measures to obtain data from communities. The public, industry, and regulators can use these data as one input to evaluating the impact that various sources have on the public health.

Regional air toxics studies benefit both the public and industry participants. These efforts provide industry, regulators, and the public a unique opportunity to work together to find answers to difficult questions. These data can provide the technically sound basis for decision-making processes.

This section has provided an overview of the rationale for conducting an air toxics monitoring program. Other factors that could affect the decision for conducting an air toxics monitoring program are driven by region-specific factors. It is, therefore, imperative for you to carefully review this document and define your specific totivations for conducting air toxics monitoring programs.

2.0 GETTING A MONITORING PROGRAM STARTED

The most critical phase of your regional air monitoring program is planning. In this phase, the direction and priorities of the program are set, the relationships and "ground rules" among the participants are established, and a foundation of cooperation and credibility is built.

To start a regional air monitoring program, you must take three steps:

- Define your objectives
- Involve others in the program
- Establish your management structure

Figure 2-1 illustrates these three key steps.

2.1 DEFINING YOUR OBJECTIVES

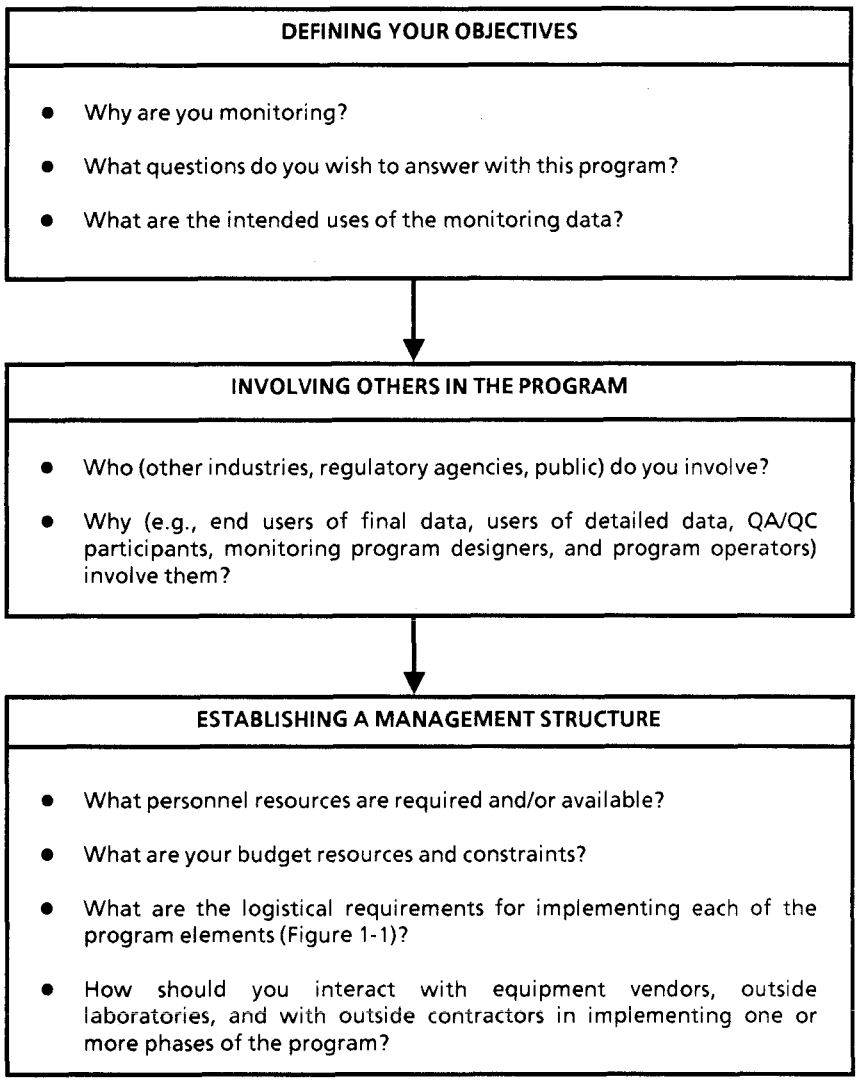
Clearly identify all of the potential objectives for the program in the beginning of the project so that the priorities for the study can be agreed upon.

The overall goal of any regional air monitoring program is to gather information about the presence and levels of airborne pollutants in the community. High-quality data are needed even if the results are used only to infer the effect of exposures to airborne pollutants. These data are essential for sound risk management.

Within these overall objectives, you will need to consider the characteristics of the region where monitoring

FIGURE 2-1

GETTING A MONITORING PROGRAM STARTED


DEFINING YOUR OBJECTIVES
• Why are you monitoring?
• What questions do you wish to answer with this program?
• What are the intended uses of the monitoring data?
INVOLVING OTHERS IN THE PROGRAM
• Who (other industries, regulatory agencies, public) do you involve?
• Why (e.g., end users of final data, users of detailed data, QA/QC participants, monitoring program designers, and program operators) involve them?
ESTABLISHING A MANAGEMENT STRUCTURE
• What personnel resources are required and/or available?
• What are your budget resources and constraints?
• What are the logistical requirements for implementing each of the program elements (Figure 1-1)?
• How should you interact with equipment vendors, outside laboratories, and with outside contractors in implementing one or more phases of the program?

will be conducted to set specific objectives for the program. You may want to consider, for example, the following questions:

- In terms of industry and/or population, is this a growth area or not?
- Is there a natural home for this monitoring network?
- Do you have to organize an industry coalition?
- What are the public concerns in the region?
- How environmentally active are the citizens groups?
- What are the particular regulatory issues in the region?
- Are new regulations being developed?
- What factors (such as climate, topography, industrial operating schedules, and public activity patterns) could affect exposures to airborne pollutants?
- Are there particular areas in the region which are suspected of having high ambient levels of airborne pollutants?
- Do they contain sensitive subpopulations?
- Where do these sensitive subpopulations live?
- What kind of data (e.g, short- or long-term) do you want?
- What studies have been conducted previously in your region and what gaps remain in the existing data base?
- What is the quality of past data and how defensible are they?
- What technical resources are available to perform or assist in the program?
- What financial resources are required and/or available for this program?

In addition, you may have other objectives for your monitoring program. These can include permitting for facility expansion, model validation studies, and emergency release evaluations.

Other issues you need to address in the beginning are how the information generated by the program will be used and who will have access to it. Ground rules must be set early to avoid future misunderstandings among project participants. Participants will expect to access results and, possibly, ongoing operations data. Nonparticipants can also inquire about the availability of and access to data. However, there is always a danger that raw data can be misinterpreted.

Resources for programs are always limited. Available resources should be concentrated on the highest priority objectives, so that the quality of results is not diluted.

The issues posed above and other considerations specific to your needs will help you make decisions on the scope of your program and the methods to be used.

2.2 INVOLVING OTHERS IN THE PROGRAM

The results of a regional air monitoring program will not be of value unless they are accepted as being valid by the general public and regulators, as well as the industrial participants. It is also true that these publics are much more likely to accept results if they have been actively included in all stages of the project.

Therefore, at the start, each party with a significant interest in the program must be involved. This involvement will ensure that the results are useful. Hence, you must consider the following questions:

Who should you involve?

All interested parties must be involved. Their objectives, once agreed upon, should be incorporated into the project planning stages to help create a focused program effort. Some typical parties include the general public, governmental bodies, industrial groups, and Chambers of Commerce. These relationships to the involvement process are described in the paragraphs below.

Identifying who in the "general public" should participate in the monitoring program is not easy. In general, you need to involve those groups or individuals whose acceptance of the study results would be most credible among other members of the public. For example, prime candidates for inclusion are public interest or environmental advocacy groups or neighborhood coalitions in areas where exposure levels are considered to be high.

Responsibility for air toxics regulations or policies generally resides with Federal, state, or local air pollution control agencies. To add credibility to your program, consider involving, or at a minimum, informing key agency staff in the regional monitoring program area. Other governmental bodies, such as regional planning commissions, may also have a stake in the monitoring results and should be considered for participation.

In addition, other industry groups or the local Chambers of Commerce are potential participants because results of the monitoring program may impact their activities.

What does "being involved" mean?

Involvement really begins with defining program objectives, as discussed in Section 2.1. If no one agrees on the goals for its program, the results will be of little use. Therefore, you should consult the program participants on key decisions such as selecting the constituents to be included in a preliminary survey and/or the the final monitoring, agreeing on the sampling schedule, and selecting the number and location of monitoring sites.

"Being involved" means having enough information, on a timely basis, about the progress, problems, and results of the program to judge whether or not it is meeting its objectives.

How are participants kept involved?

Involvement is largely a matter of your establishing relationships and maintaining communications. Once the participants are identified, make every effort to maintain continuity of personnel so that working relationships and credibility are established and maintained. Send participants information regularly and on a timely basis. Furthermore, in the planning phase and at key points throughout the project, you should meet with participants regularly to discuss key issues, review results, or solve problems encountered. The public at large and opinion leaders can be kept informed via open meetings and press releases. In this regard you should designate a project participant as the program's communications coordinator.

2.3 ESTABLISHING A MANAGEMENT STRUCTURE

A regional air toxics monitoring program is a complex undertaking. Depending on program objectives, a program can last from several days to many years. Costs of the program can be considerable (see Section 7.0). It is necessary, then, for you to establish a program management structure to make decisions regarding the monitoring program, implement them, and administer funds to accomplish the program objectives. A number of mechanisms are available to administer the monitoring program including:

- A management committee, composed of representatives of contributing sponsors.
- A corporation formed specifically to run the program (as was done in the Houston Regional Monitoring Project).
- An outside party, such as a Chamber of Commerce, which could collect and disburse funds, with management direction coming from a committee of representatives of contributing sponsors.

Typically, final decision-making power regarding allocation of resources resides with those who are financing the study. However, as described in Section 2.2, you should closely consult with a broad range of participants so that study results can be credibly communicated and be accepted by the various publics. Funding for the program may come entirely from industry or from other sponsors, regulatory agencies, community groups, or environmental trust funds.

Responsibilities for planning and implementing tasks are outlined in Figure 1-1. These tasks are discussed in detail in Chapters 3.0-7.0. Once program objectives are defined and the management structure is established and operating, your management group must develop a monitoring program plan. Even after the monitoring program plan is written, your management team must continue to follow the plan implementation to ensure that the program's objectives are met. Note that all of the individual items in Figure 1-1 will come into play at some point during the project.

Be aware that if you do not continue to follow the plan throughout the project, its data and results may not be defensible.

3.0 DEVELOPING THE MONITORING PLAN AND METHODOLOGIES

The monitoring plan provides the detailed design for a regional air toxics monitoring program. It is the design that sets the boundaries for the program by defining the elements involved through a well thought-out process.

By developing a monitoring plan, you will answer the following key questions:

- What constituents will be monitored?
- How many monitoring stations will be involved and where will they be located?
- What is the sampling duration and frequency and the program length?
- What sampling and analysis methods will be employed?
- Who and what will be the resource requirements involved?

Answers to these questions early in the program save time and money by streamlining the process, eliminating unneeded steps, and avoiding pitfalls.

3.1 OVERVIEW OF PLAN ELEMENTS

A good monitoring plan consists of several steps including those shown in Figure 3-1. A brief discussion of each of these steps occurs in the following paragraphs.

In developing a monitoring plan, first select the constituents to be monitored. Section 3.2 discusses factors to be considered in developing this list.

Secondly, define the duration and frequency of monitoring to meet specific program needs. Section 3.3 provides a discussion of this subject. Table 3-1 provides general guidelines for program length, sampling duration and frequency by program objectives.

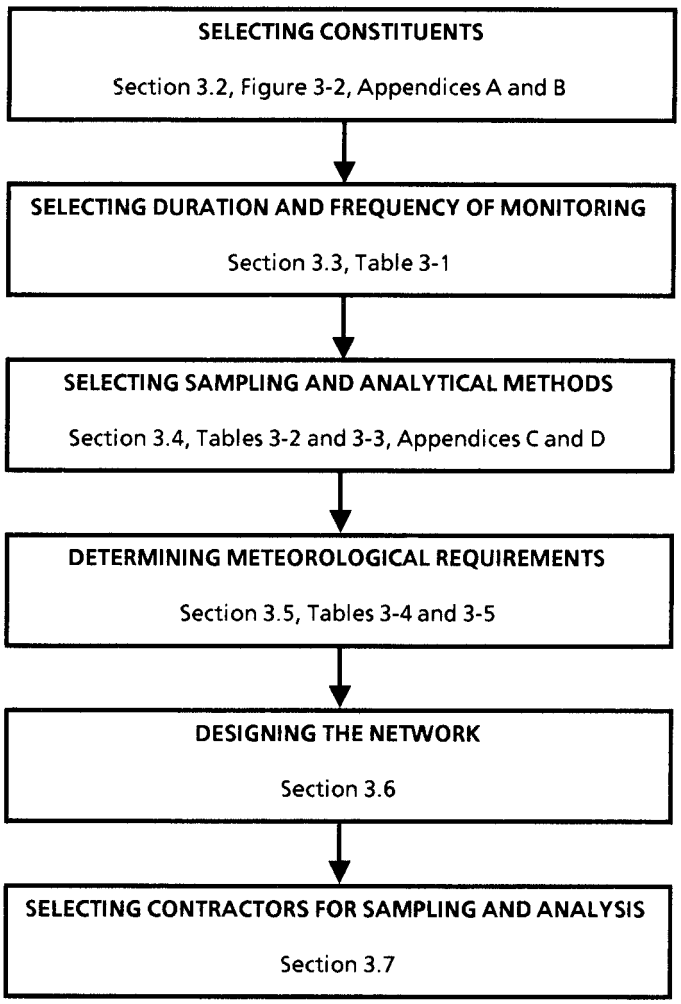
Third, a key element of the monitoring plan is the selection of sampling and analysis methods most suitable for your program. This selection is based on the program objectives, resources, and constraints. Section 3.4 provides a discussion of sampling and analysis methodologies. Details are provided in Appendices C and D.

In addition to the air monitoring methods, the meteorological monitoring requirements associated with each air monitoring program are important. A discussion of these requirements is included in Section 3.5.

Next comes the design of the network which is described in Section 3.6. This section covers the number and locations of monitoring stations, the siting of air monitoring and meteorological stations, the use of models to select monitoring sites, and network design for dispersion model validation.

Finally, the selection of contractors for performing air sampling and analysis is discussed in Section 3.7. Also, the elements associated with such a selection process are included in this section.

FIGURE 3-1
KEY ELEMENTS OF A REGIONAL AIR TOXICS MONITORING PROGRAM


SELECTING CONSTITUENTS
Section 3.2, Figure 3-2, Appendices A and B
SELECTING DURATION AND FREQUENCY OF MONITORING
Section 3.3, Table 3-1
SELECTING SAMPLING AND ANALYTICAL METHODS
Section 3.4, Tables 3-2 and 3-3, Appendices C and D
DETERMINING METEOROLOGICAL REQUIREMENTS
Section 3.5, Tables 3-4 and 3-5
DESIGNING THE NETWORK
Section 3.6
SELECTING CONTRACTORS FOR SAMPLING AND ANALYSIS
Section 3.7

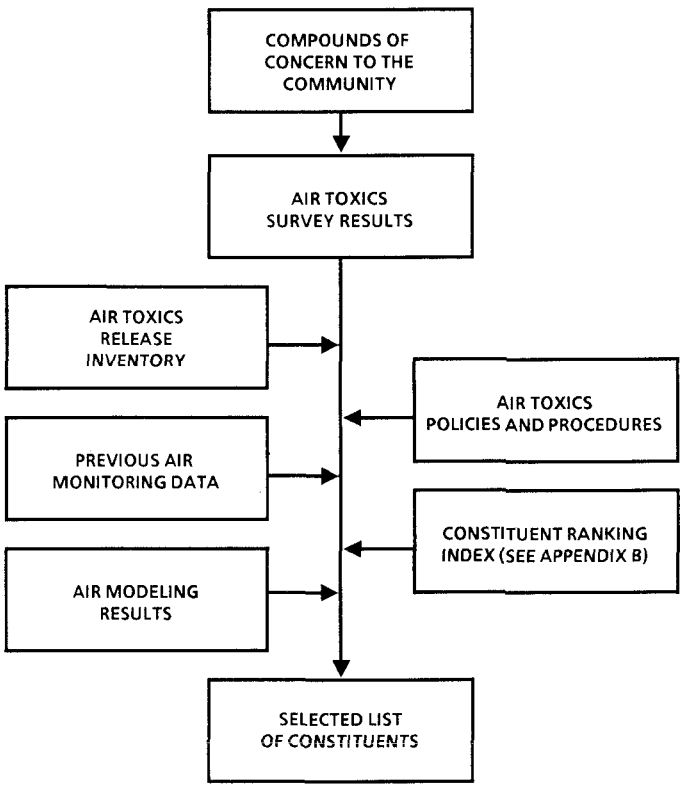
3.2 SELECTING CONSTITUENTS OF INTEREST

Once a decision has been made to conduct a regional air monitoring program, you have to establish a list of constituents to be analyzed. Figure 3-2 outlines the process for selecting constituents.

The starting point is the list of chemicals of concern to the community. Not all airborne pollutants are measurable using existing techniques. To aid the reader, the lists of pollutants that are on the U.S. Environmental Protection Agency (EPA) lists of volatile organics quantified in the Toxic Air Monitoring Stations (TAMS) program and the Urban Toxics Monitoring Program are provided in Appendix A. These lists include all of the compounds which EPA considers to be amenable to analysis. EPA uses this list extensively in its air monitoring programs. Appendix A also includes the Houston Regional Monitoring (HRM) list of air pollutants. This list includes the compounds analyzed under the HRM program.

To confirm the presence of the chemicals in Appendix A in your region, it is recommended that you consider conducting a short-term air monitoring survey to collect a limited number of samples and analyze them for all the constituents included in this appendix. These results will provide preliminary insight on the presence and magnitude of the detected constituents.

FIGURE 3-2
SELECTING MONITORING CONSTITUENTS


COMPOUNDS OF CONCERN TO THE COMMUNITY
AIR TOXICS SURVEY RESULTS
AIR TOXICS RELEASE INVENTORY
AIR TOXICS POLICIES AND PROCEDURES
PREVIOUS AIR MONITORING DATA
CONSTITUENT RANKING INDEX (SEE APPENDIX B)
AIR MODELING RESULTS
SELECTED LIST OF CONSTITUENTS

The Superfund Amendments Reauthorization Act (SARA) 313 list contains some components that are very difficult to measure. For some components, new sampling and analytical methods are needed. In fact, for some pollutants, the monitoring difficulties are cost prohibitive.

If the monitoring results for a large number of the measured constituents are below the detection limits, you can reduce the list of constituents to be monitored. Otherwise, one may choose to continue monitoring all constituents listed in Appendix A.

Since the primary goal of the program is to identify concentrations of air pollutants in the community, the selected list of constituents for monitoring should reflect local concerns and issues. To meet this objective, it is recommended that you evaluate the following:

- Community concerns regarding certain types of air toxics. This should be a key factor in the selection process of constituents to be monitored.
- Air toxics release inventories filed under the requirements of the "Toxic Chemical Release Reporting; Community Right-to-Know," (40 CFR Part 372 subpart D). EPA has computerized these inventories, and these data are accessible to the public. Such data will provide information on air toxics releases to the atmosphere from reporting industries. You can obtain additional release information from Federal and state agencies. In addition, EPA has information on estimates of air toxic constituents emitted from mobile sources.
- Air monitoring data available from previous monitoring programs in the monitored region. These data would identify potential air toxics' constituents and their estimated concentrations. Use such data with caution because changes in demographics may have occurred after these data were collected. Section 3.8 contains several references on previous monitoring programs.[1, 2, 3]
- Results of air dispersion modeling. Such results provide information on calculated levels of air toxics at different locations within the community relative to their releases.
- Lists contained in state and local air toxics policies and procedures.
- Constituents Ranking Index (CRI) values. These can provide important information for establishing priorities for air toxics constituents as a part of the selection process. The ranking process is explained in Appendix B. The CRI is the ratio of a constituent's calculated or measured air concentration to a health-oriented number derived from animal experimental data. The derived ratios are used to rank the constituents as explained in Appendix B. Other ranking methods are available for the selection of the list of target constituents.

Examples include *The Modified Hazardous Air Pollutant Prioritization System (MHAPPS)*[4] *and Source Category Ranking System*[5].

Using these factors, together with the results of the air toxics survey monitoring, can provide you the basis for determining whether your regional air toxics program will address all the constituents included in Appendix A, add more constituents, or reduce the list to fit your specific regional situation. The selected list of constituents should be specific to each study area.

3.3 SELECTING DURATION AND FREQUENCY OF MONITORING

Recommendations for sampling duration, frequency, and length of the monitoring program are summarized in Table 3-1 by program objectives. Primary program objectives include air toxics survey monitoring, and long-term monitoring to establish community concentrations of air toxics. Other program objectives include, for example, short- or long-term effect studies, compliance studies, or permitting studies.

Actual sampling duration, frequency, and monitoring program length will depend on your specific project objectives and on your available project resources. A representative number of air samples must be collected during the monitoring program to provide a reasonable data base. The number of representative samples depends on many factors. A simple, statistical analysis may not provide a good basis for determining this number. The recommendations specified in Table 3-1 are based on the following factors:

- Frequencies usually adopted in monitoring programs for criteria air pollutants involving the use of time-integrated samplers. A minimum of one sample every six days is collected to provide random weekday and weekend sampling.
- Use of continuous monitoring for program objectives that require short sampling durations.
- The resource requirements for laboratory analysis for organic and inorganic compounds.
- Quality assurance/quality control requirements such as collocated field and trip blank samples, and spike samples.

Samples taken over a very short period of time (a few minutes or so) do not represent average concentrations of airborne pollutants. High variability could occur over short periods of time. Samples taken during regional air monitoring surveys should be averaged over at least one hour and, preferably, over a longer period of time.

You should tailor the general guidance presented in Table 3-1 to your specific applications.

In most cases, the 24-hour sampling duration is highly recommended for long-term monitoring for both organic and inorganic constituents. Use the 8-hour sampling duration for compliance studies, acute health effects studies, or preliminary survey studies. For compliance and health studies this duration is used to maintain consistency with the 8-hour TLV values. Sampling for air toxicity monitoring survey studies is done for periods of 8 hours to provide more data points during a short period of time.

Use a 12-hour sampling duration for determining the effect of daytime and nighttime meteorology on air toxic concentrations. This sampling duration covers nighttime thermal inversions.

Apply the 3-hour sampling duration to several objectives. Use it during ozone formation studies, when the period between 6:00 a.m. to 9:00 a.m. is very critical. Apply the 3-hour sampling duration to cover meteorological events such as nighttime thermal inversions or on-shore breezes, or unusual events associated with the operation of industrial facilities. The 3- to 8-hour sampling periods also are important when sorbent tubes are used and breakthrough of constituents trapped in the tubes could occur. Breakthrough could be a factor when Tenax tubes are used in the sampling program.

The recommended program lengths in Table 3-1 provide a reasonable data base that can be used in the application under consideration. For most of the program objectives in Table 3-1, you should obtain a minimum of 30 samples. If the program lasts less than a year, this will result in an increased sampling frequency.

For model validation study, 24-hour integrated samples are generally suitable. Short-term samples, such as 1-hour averages, can closely track effects of variability in wind direction. However, these advantages are frequently offset by the need to deploy more samplers to increase the likelihood of sampling in the contaminant plume, and by increased laboratory cost for more samples.

When the program lasts less than a full year, identify any "reasonable worst-case" period for the monitoring program. This period is characterized by high ground-level concentrations of air toxic releases from industrial and nonindustrial sources.

Use air emission release-rate models and atmospheric dispersion models to identify reasonable, worst-case exposure conditions (i.e., to quantitatively account for the above factors). For a worst-case application, limit the modeling effort to a screening/sensitivity exercise to obtain "relative" results for a variety of sources and meteorological scenarios. Consider only those meteorological parameters of greatest significance (e.g., temperature, wind speed, and stability).

Cost is a major consideration in selecting the frequency and duration of the sampling program. Overall

TABLE 3-1

RECOMMENDED PROGRAM SAMPLING DURATION AND FREQUENCY AND PROGRAM LENGTH BY OBJECTIVES

Program Objectives	Sampling Duration					Sampling Frequency					Program Length				
	1 Hour	3 Hours	8 Hours	12 Hours	24 Hours	≦ 7 Days	30 Days	90 Days	1 Year	> 1 Year	≦ 7 Days	30 Days	90 Days	1 Year	> 1 Year
I PRIMARY OBJECTIVES															
• Survey Studies		O	R	O	O	Daily(3)	Every other day	Once in 3 days			O	R	R		
• Establish Community Concentrations		O			R			Once in 3 days	Once in 6 days	Once in 6 days			O	R	O
II OTHER OBJECTIVES															
• Long-Term Effects Studies					R			Once in 3 days	Once in 6 days	Once in 6 days			O	R	O
• Short-Term Effects Studies	O	O(1)	R	O(2)			Every other day	Once in 3 days	Once in 6 days			O	R	O	
• Refine Source-Receptor Relationships		O			O			Once in 3 days	Once in 6 days	Once in 6 days			O	O	O
• Compliance Studies	O	O	R		O		Every other day	Once in 3 days	Once in 6 days	Once in 6 days		O	O	O	O
• Model Validation Studies	O				R	Daily(3)		Once in 3 days	Once in 6 days		O		O	O	
• Permitting for Industry Future Expansion	O				R	Daily(3)		Once in 3 days	Once in 6 days		O		O	O	
• Emergency Release Evaluations	O	O				Daily(3)					R				

R = Recommended
O = Optional

(1) Applicable to ozone precursor studies
(2) Applicable to diurnal effects studies
(3) Multiple samples during each day

operating costs for a program are, in large measure, directly proportional to the numbers of samples collected. Section 7.0 illustrates the effects that the program's duration and sampling frequency can have on costs.

Select sampling periods in a way that will satisfy regulations and public opinion. This kind of scheduling will help avoid criticism that sample periods do not represent industrial practices or other activities in the community. Address the potential problem by adopting a random schedule with the minimum practical advance notice. Also, consider collecting more samples than are needed for the data base, and then decide at a later time, which samples will be analyzed. (See Section 3.4 for a discussion of sample holding time limitations.)

3.4 SELECTING SAMPLING AND ANALYTICAL METHODS

Alternative air toxic monitoring techniques for regional air monitoring programs are classified as follows:

- Time-integrated techniques.
- Near-real-time techniques.
- Screening-level techniques.

Time-integrated air monitoring methods are applicable when high-quality data are required and the short-term, temporary variability of concentrations is not important. In fact, these methods are the most suitable for regional air monitoring programs. Table 3-2 presents a listing of typical time-integrated monitoring techniques. A brief description of these techniques, the EPA method number, and the type of compounds detected are included in Table 3-3. Additional details are included in Appendix C.

U.S. EPA considers canisters for collecting whole-air samples on a time-integrated basis as the method of choice, but not the only acceptable method, for sampling volatile organic compounds. It is the recommended method for regional air monitoring programs. Sorbent tubes and Tedlar® bags should be considered as second and third choices, respectively, for collecting volatiles on a time-integrated basis. You should be aware of the limitations associated with these methods. They include a short holding time from sampling to analysis and a higher risk of sample losses and contamination.

Near-real-time air toxic monitoring techniques are a second choice alternative to time-integrated methods. These techniques can provide reasonably accurate information (in ppbs) on ambient air quality of organic compounds in the gas phase. They also use a combination of air sampling and a near-real-time analytical analysis without the use of offsite laboratory facilities. The analysis is performed with field portable gas chromatograph (GC) systems (see examples in Table 3-2).

Limitations of the near-real-time methods included in the following:

TABLE 3-2

AN OVERVIEW OF AIR TOXICS MONITORING/SAMPLING TECHNIQUES

Technique Classification	Category of Monitoring/Sampling Method	Detection Limit	Compounds Detected	Monitoring/Sampling Mode
TIME-INTEGRATED				
Gas Phase:	• Traps (sorbents and cryogenics) and laboratory analysis	Fraction of a ppb to ppb	Many organic compounds by chemical species	Historical-integrated
	• Whole-air samplers (canisters and bags) and laboratory analysis	Fraction of a ppb to ppb	Many organic compounds by chemical species	Historical-integrated
	• Liquid impingers	Fraction of a ppb to ppb	Aldehydes, ketones, phosgene, cresol/phenols	Historical-integrated
Particulate Phase:	• High-volume samplers with glass fiber filter, membrane filter or Teflon filter	$\mu g/m^3$	Inorganics	Historical-integrated
	• High-volume samplers with glass fiber filter and polyurethane foam*	$\mu g/m^3$	PCBs and other semi-volatile organic species	Historical-integrated
NEAR-REAL-TIME				
Gas Phase:	• Portable field GC analyzers with constant-temperature oven	ppb	Limited list of organic compounds by chemical species	Historical-integrated
	• Field GC laboratory	ppb	Limited list of organic compounds by chemical species	Historical-integrated
SCREENING				
Gas Phase:	• Total Hydrocarbon (THC) Analyzers	ppm	Most organics but not by chemical species	Realtime-continuous
	• Colorimetric gas detection tubes and monitors	ppm	Various organics and inorganics for a specific chemical species	Historical-integrated
	• Electrochemical alarm cells	ppm	Various organics for a specific chemical species	Realtime-continuous
Particulate Phase:	• Portable pumps with filters	mg/m^3	Most inorganic compounds	Historical-integrated
	• Portable pumps with filters and special plugs	mg/m^3	Semi-volatile chemical species	Historical-integrated

* Polyurethane foam (PUF) plug is designed to collect semi-volatile organic gases.

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TABLE 3-3
A SUMMARY OF TIME INTEGRATED MONITORING TECHNIQUES FOR ORGANICS AND INORGANICS IN AIR

Technique †	EPA Method Number	Type of Compounds
ORGANIC COMPOUNDS – TRAPS		
Sorption onto Tenax GC Packed Cartridges using low-volume pump and GC/MS Analysis.	TO-1	Volatile, nonpolar organic (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C, in gas or vapor phase.
Sorption onto Carbon Molecular Sieve packed cartridge using low-volume pump and GC/MS analyses.	TO-2	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of −15° to + 120°C, in gas or vapor phase.
Collection of accurately known volume of air into cryogenically cooled trap in the field and GC/FID or ECD analyses.	TO-3	Volatile, nonpolar organics having boiling points in the range of −10° to + 200°C, in gas or vapor phase.
Sorption onto polyurethane (PUF) using high-volume sampler and GC/ECD analysis.	TO-4	Organochlorine pesticides and PCBs.
Sorption onto Thermosorb/N packed cartridges using low-volume pump GC/MS analysis.	TO-7	N-Nitrosodimethylamine in gas phase.
Sorption onto PUF using low-volume or high-volume pump and high resolution Gas Chromatography/ High Resolution Mass Spectrometry (HRGC/HRMS).	TO-9	Dioxin.
Sorption onto PUF using low-volume sampler and Gas-Liquid Chromatography coupled with ECD.	TO-10	Organochlorine pesticides.
Sorption onto prepacked silica gel cartridge coated with acidified dinitrophenylhydrazine (DNPH) using low-volume pump and High Performance Liquid Chromatography (HPLC).	TO-11	Formaldehyde.
Sorption to a combination of quartz filter and a XAD-2 or PUF cartridge using high-volume sampler and GC with Flame Ionization (FI) or MS detection or HPLC.	TO-13	Benzo(a)pyrene, [B(a)P] and other polynuclear aromatic hydrocarbons.
ORGANIC COMPOUNDS – WHOLE AIR SAMPLERS		
Whole-air samples are collected in a SUMMA passivated stainless steel canister and high resolution GC coupled with mass specific spectrometer (GC MS-SIM or GC-MS-SCAN).	TO-14	Volatile, nonpolar organic (e.g., aromatic hydrocarbons) chlorinated hydrocarbons having boiling points of −30°C to about 215°C.
Whole-air samples extracted directly from ambient air and analyzed using cryogenic preconcentration and direct flame ionization detector (PDFID), or air samples are collected in a canister and analyzed by PDFID.	TO-12	Non-methane organic compounds (NMOC).
Whole-air samples are collected in Tedlar bags and subject to GC/FID or ECD analysis or high-resolution GC compiled with MS-SIM or MS-SCAN.	Modified TO-3 or TO-14	TO-14 or TO-3 Compounds.
ORGANIC COMPOUNDS – LIQUID IMPINGERS		
Dinitrophenylhydrazine Liquid Impinger sampling using a low-volume pump and High Performance Liquid Chromatography/UV analysis.	TO-5	Aldehydes and Ketones
Aniline liquid impinger sampling using a low-volume pump and HPLC analysis.	TO-6	Phosgene.
Sodium Hydroxide Liquid Impinger sampling using a low-volume pump and HPLC analysis.	TO-8	Cresol/Phenol.
INORGANIC COMPOUNDS – FILTER SAMPLERS		
High-volume sampler and Atomic Absorption (AA) or Inductive Coupled Plasma (ICP).	40 CFR Part 50 Appendix B*	Metals in particulate phase.
PM-10 High Volume sampler and AA or ICP.	40 CFR Part 50 Appendix J*	Inhalable metals in particulate phase (up to 10 microns in diameter).
High-volume sampler.	40 CFR Part 50 Appendix B	Total suspended particulate (TSP).
PM-10 High-volume sampler.	40 CFR Part 50 Appendix J	Inhalable particulate up to 10 microns in diameter.

† Additional details are included in Appendix C.
* For sampling methodology only.

- The list of chemical species that can be accommodated is shorter than the one handled by a fully equipped, offsite laboratory.
- Only an uncomplicated matrix of chemical species can be analyzed.
- As field techniques, these methods lack the ability to comply with the comprehensive quality assurance/quality control (QA/QC) procedures used by a certified offsite laboratory.

Screening air monitoring techniques (such as total hydrocarbon analyzers, colorimetric gas detection tubes, and industrial hygiene methods) are generally inexpensive, but are only successful for measuring relatively high detection levels (i.e., in the ranges of parts per million for gaseous contaminants and milligrams per cubic meter for particulates). Frequently, screening air monitoring techniques provide near-real-time results in the field. Alternative survey-level techniques are presented in Table 3-2. Screening techniques are quite limited in the number of constituents that can be evaluated concurrently. Hence, these techniques are most effective for air monitoring near the source to confirm the presence of an air release and to provide information to support the development of specifications for a more refined monitoring program. Screening techniques are not recommended for use in regional air monitoring programs.

Base your selection of air monitoring methods and equipment on a number of factors, including the following:

- Physical and chemical properties of compounds.
- Relative and absolute concentrations of compounds.
- Relative importance of various compounds in program objectives.
- Method performance characteristics.
- Potential interferences present at the monitoring site.
- Time resolution requirements.
- Cost restraints.

Organic and inorganic constituents are monitored by different methods. Various methods may also be required for monitoring either organics or inorganics, depending on the constituents and their physical/chemical properties. Whether a compound occurs primarily in the gaseous phase or is found absorbed to solid particles or aerosols also affects your choice of monitoring techniques.

Sampling methodologies for PCBs and other semivolatile organic constituents, as well as for inorganics in the form of particulates, are also included in Table 3-2.

Laboratory analytical techniques must provide for the positive identification of the components and the accurate and precise measurement of concentrations. This generally means that the preconcentration and/or storage of air samples are required. Therefore, methods chosen for time-integrated monitoring usually require a longer analytical time period, more sophisticated equipment, and more rigorous quality assurance (QA) procedures.

Table 3-4 presents a comparison of advantages and

TABLE 3-4

COMPARISONS OF REGIONAL AIR MONITORING TECHNIQUES

Technique	Advantages	Disadvantages
Time-Integrated	• Sampling equipment not complex • Standard approach used for monitoring air pollutants	• Laboratory costs can be expensive for numerous samples • Short-term temporal concentration variations not defined
Near-Real-time	• Results available immediately • Can be cost-effective for high sampling frequency • Provides information on temporal concentration variations	• Equipment is complex • Number of sampling constituents limited • Accuracy can be impaired by interferences
Survey	• Simple to use • Inexpensive	• High detection levels • Matrix interferences a major problem

disadvantages of alternative monitoring techniques. A list of references and tables which provide additional guidance on regional air monitoring methodologies is presented in Appendix C. Tables C-2 through C-10 summarize time-integrated sampling and analysis techniques for organic and inorganic air pollutants. These methods are recommended for regional air monitoring.

Table C-11 in Appendix C includes information on emerging technologies for regional air monitoring. These technologies are not recommended for use in regional air monitoring at this time, but are applicable to some special purpose studies. This section, along with the data included in Appendix C, provides useful guidance in the selection process for regional air monitoring techniques.

3.5 DEFINING METEOROLOGICAL REQUIREMENTS

The number of meteorological stations associated with regional air monitoring programs depends on specific local conditions such as topography (land/water interface), the distance between individual monitoring stations, and program objectives. A meteorological station located next to each air sampling station is recommended. However, you could modify this recommendation, depending on your specific local conditions. For example, one meteorological station could be sufficient if the following conditions exist: a flat or gently rolling topography with no air/water interface, no major obstruction interferences, short distances between stations (a mile or less), and no major emphasis on the determination of upwind and downwind concentrations.

Classes of meteorological monitoring parameters for regional air monitoring applications include:

- Primary parameters including wind direction, wind speed, sigma theta (i.e., the horizontal wind direction standard deviation, which is an indicator of atmospheric stability), and solar radiation.
- Secondary parameters including temperature, precipitation, humidity, and atmospheric pressure.

Primary parameters represent regional dispersion conditions and should be included in *all* meteorological monitoring programs. Secondary parameters represent emission conditions.

Currently, the use of sigma theta in determining atmospheric stability is an EPA acceptable method. EPA is considering the use of the vertical temperature difference, delta T, in conjunction with net solar radiation to determine atmospheric stability. Once EPA makes delta T a part of the method for determining atmospheric stability, it should be integrated in meteorological stations for regional air monitoring.

Recommended meteorological monitoring system accuracies/resolutions and sensor response characteristics are summarized in Tables 3-5 and 3-6, respectively.

Field equipment used to collect meteorological data can range in complexity from a very simple analog or mechanical pulse counter data-logging system, to a microprocessor-based data logging system. Combine these approaches for your regional air monitoring program. This recommendation is not expensive and facilitates the convenient collection of meteorological hourly-averaged data that can be easily processed, using personal computers (PCs). Chart recorders provide a low-cost backup system, if the digital data are not available.

You should conduct a meteorological survey (i.e., short-term data collection) to support air monitoring network design. Exceptions to this practice would include areas that have historical, onsite meteorological data or flat-terrain areas where representative offsite data are available. The duration of the meteorological survey should range from 2 to 6 weeks, depending on the objectives and the design elements of the monitoring program. In many cases, for planning purposes, you may use historical, offsite data to estimate seasonal effects if the air monitoring program is scheduled to last for more than a few months.

Additional recommendations on meteorological measurements can be obtained from a number of U.S. EPA documents.[6, 7, 8, 9]

TABLE 3-5

RECOMMENDED SYSTEM ACCURACIES AND RESOLUTIONS

Meteorological Variable	System Accuracy	Measurement Resolution
Wind Speed	± (0.2 m/sec + 5% of observed)	0.1 m/sec
Wind Direction	± 5 degrees	1 degree
Ambient Temperature	± 0.5°C	0.1°C
Dew Point Temperature	± 1.5°C	0.1°C
Precipitation	± 10% of observed	0.3 mm
Pressure	± 3 mb (0.3 kPa)	0.5 mb
Time	± 5 minutes	----

Source: U.S. EPA Onsite Meteorological Program Guidance for Regulatory Modeling Applications[9].

3.6 DESIGNING THE NETWORK

Number and Location of Monitoring Stations

Consider the following key factors when selecting the locations and the number of monitoring stations for regional air monitoring programs:

- Results of air dispersion modeling for the region using an atmospheric dispersion model applicable to the sources and the region under consideration.
- Receptor characteristics (population centers, residential communities, sensitive receptors such as hospitals and schools, and environmental locations, locations of calculated high concentrations of airborne pollutants).
- Environmental characteristics (e.g., meteorology and topography). Meteorological variables affecting monitoring network design include wind direction, wind speed, and atmospheric stability. Use these parameters to define prevailing wind patterns and to characterize local dispersion conditions considering source-receptor relationships. Consider conditions such as nighttime thermal inversions and downhill drainage flow that are conducive to high-ground-level concentrations of the toxic chemicals released from the facility or industrial sources involved. Topographical effects on plume dispersion include valley flow and plume dispersion in complex terrain. Nearby water bodies could introduce land/water interface and associated onshore flow (breeze) effects.
- Number and locations of sources and their characteristics. Source characteristics include emission rate, type of source (point, area, volume or line), type of emissions (fugitive or not), and nearby structures that could cause wake and plume downwash effects.

These factors can be formulated and incorporated into a dispersion modeling scheme to calculate ground level concentrations of airborne pollutants for the receptor grid of interest. Results of the dispersion modeling provide locations of calculated high, short-term (up to 24-hour), average concentrations, frequency of occurrence, and locations of maximum, long-term (monthly, seasonal, and annual), average concentrations.

The compiled modeling results, together with the factors listed above, serve as the primary basis to determine the number and locations of monitoring stations.

You should also account for the available resources and the constraints of the program. Table 3-7 provides general guidance for selecting the minimum stations for regional air monitoring and their locations. The actual number and locations should be determined on a case-by-case basis considering region-specific factors, project objectives, resources, and budget constraints.

Some of region-specific factors that could increase the number and locations of your monitoring stations are:

- Type of sources involved. Simple sources consist usually of well-defined emission points and include several stacks that do not have nearby obstructions. Complex sources involve large numbers of sources scattered over a wide area and/or sources that do not have well-defined emission points. Complex sources have emissions from roof monitors, vents, valves, and other components and are defined as fugitive sources. These sources also include irregular structures that exist near emission locations. Complex sources will require more monitoring stations than simple sources.
- Size of the region involved and community locations.
- Topography coupled with wind flow and land/water interface, together with wind flow conditions, will require additional monitoring stations at locations of anticipated high concentrations.
- Areas of high traffic density and locations of major arteries could require additional monitoring stations.
- Locations of community, commercial, and light industry activities could require additional monitoring stations.

TABLE 3-6

RECOMMENDED RESPONSE CHARACTERISTICS FOR METEOROLOGICAL SENSORS

Meteorological Variable	Sensor Specification(s)
Wind Speed	Starting Speed ≤ 0.5 m/sec; Distance Constant ≤ 5m
Wind Direction	Starting Speed ≤ 0.5 m/sec @ 10° Deflection; Damping Ratio 0.4 to 0.7; Delay Distance ≤ 5m
Temperature	Time Constant ≤ 1 minute
Dew Point Temperature	Time Constant ≤ 30 minutes; Operating Temperature Range -30°C to + 30°C

Source: U.S. EPA On-Site Meteorological Program Guidance for Regulatory Modeling Applications[9].

TABLE 3-7

GUIDANCE FOR SELECTING THE NUMBER AND LOCATIONS OF MONITORING STATIONS FOR REGIONAL AIR MONITORING PROGRAMS

Source Type	Minimum Number of Monitoring Stations[1][2]	Location
Simple Sources	3	2 at downwind locations, preferably in residential areas where high concentrations are anticipated with a reasonable frequency of occurrence 1 at upwind location from the sources preferably in a residential area
Complex Sources	4-6	3-4 at downwind locations with similar characteristics as for simple sources 1-2 at upwind locations from the sources, preferably in residential areas

1. For sources near topographical features: add two stations to each of the above cases at locations of anticipated high concentrations with high frequency of occurrence (plume impaction at high terrain, location with drainage flow), preferably in residential areas.

2. For sources near bodies of water: add two stations to each of the first cases at locations of anticipated high concentrations with high frequency of occurrence (plume fumigation region), preferably in residential areas.

TABLE 3-8

A SUMMARY OF KEY PROBE SITTING CRITERIA FOR AIR MONITORING STATIONS

Factor	Criteria
Vertical spacing above ground	• Representative of the breathing zone and avoiding effects of obstruction, obstacles, and roadway traffic. Height of probe intake above ground is in general, 2-3m and 2-15m in the case of nearby roadways. • About 1m or more above the structure where the sampler is located.
Horizontal spacing from obstruction and obstacles	• Minimum horizontal separation from obstructions such as trees is >20m from the dripline and 10m from the dripline when the trees act as an obstruction. • Distance from sampler inlet to an obstacle such as a building must be at least twice the height the obstacle protrudes above the sampler. • If a sampler is located on a roof or other structures, there must be a minimum of 2m separation from walls, parapets, penthouses, etc. • There must be sufficient separation between the sampler and a furnace or incinerator flue. The separation distance depends on the height and the nature of the emissions involved.
Unrestricted airflow	• Unrestricted airflow must exist in an arc of at least 270 degrees around the sampler, and the predominant wind direction for the monitoring period must be included in the 270 degree arc.
Spacing from roads	• The sampler must be located far enough away from nearby roadways to avoid the effect of dust re-entrainment and vehicular emissions on the measured air concentrations. • Sampler should be placed at a distance of 5-25m from the edge of the nearest traffic lane on the roadway, depending on the vertical placement of the sampler inlet, which could be 2-15m above ground.

After you have collected, analyzed, and assessed one year's worth of data, you can expand the regional air monitoring network to accommodate some of the region-specific factors addressed above.

Siting Air Monitoring and Meteorological Stations

It is likely that one main reason to perform regional air monitoring is to collect high quality data for use in decision making. Therefore, the placement of both air monitoring and meteorological stations is critical to obtain data that meet data recovery requirements. Currently, for permitting purposes, EPA requires data recovery rates of 80 percent for air quality data and 90 percent for meteorological data. Any regional air monitoring system established should plan to meet or exceed these requirements to ensure credibility of the results.

Placement of air monitoring and meteorological stations must conform to a consistent set of criteria and guidance. Correct placement ensures data comparability and compatibility. A detailed set of probe siting criteria for ambient air monitoring and meteorological programs is given in EPA *Ambient Monitoring Guidelines for Prevention of Significant Deterioration.*[8]

Key siting factors include the following:

- Vertical placement above ground
- Horizontal spacing from obstructions and obstacles
- Unrestricted air flow
- Spacing from roads
- Site accessibility
- Power availability
- Site security

Table 3-8 includes a summary of the key criteria associated with these siting factors for air monitoring stations. You should use the information included in Table 3-8 as part of the monitoring network design. This will ensure that the monitoring program provides representative and unbiased data. However, site-specific constraints could make it very difficult for you to meet all siting criteria. For example, the occurrence of buildings around a candidate monitoring site would make siting very difficult. Therefore, you should use the information in Table 3-8, coupled with a balanced evaluation by an experienced air quality and meteorology specialist. The following paragraphs discuss key principles you should consider when siting air monitoring and meteorological stations.

For a monitoring site area with no major obstructions and obstacles, the air sampler intake should be at the breathing-zone height of about 2-3 meters above ground. For a site with nearby roadways, however, intake placement should take into account the effects of road dust re-entrainment and vehicular emissions.

To ensure a representative exposure, the meteorological stations should be located at distances of at least 10 times the heights of any nearby obstructions.

In most cases, it is recommended that meteorological sensors be placed 10 meters above ground (for wind and stability data) and instruments for measuring parameters, such as ambient temperature and precipitation, be placed 2 meters above ground. The use of a portable meteorological system mounted on a tripod is possible for certain applications, such as short duration studies.

Siting constraints, including power availability, site access, nearby obstructions, and site security, are integral parts of the monitoring site selection process.

In most monitoring applications, a reliable external power source is critical. Therefore, if power is unavailable, a candidate site should be excluded from further consideration.

Easy access to the site is required to ensure proper program implementation. An access road should be prepared, if required. Or a second candidate site should be used, if it is more accessible.

Avoid selecting a monitoring site in the vicinity of nearby obstructions that block air flow, such as buildings or tall trees; this is particularly important in urban areas.

Site security is an important factor in protecting the integrity of the program. Sites should have fences and lights. If possible, equipment should be placed in instrument shelters. In addition, monitoring sites could be located on residential properties where owners can provide some protection for the equipment.

Site Preparation Requirements

Once monitoring sites have been selected, you must prepare them to accept the monitoring instruments. The equipment used for VOC and particulate sampling has its own housing and does not require special instrument shelters. If you want to monitor for gaseous criteria air pollutants, (SO_2, NO_x, CO, O_3), you need a temperature-controlled shelter at each site.

You must prepare platforms for mounting the VOC samplers and particulate samplers (if required). These platforms are needed to keep samplers at a proper height above the ground.

You must also build a tower foundation for the installation of the meteorological station. The size of the foundation can vary, based on the type of tower employed and the type of soil involved. Meteorological stations usually are provided with their own housing for the electronics and data logger and, in general, do not require additional shelters.

An integral part of the site preparation includes the supply of reliable electricity. In general, the electricity supply requirements are 110-volt AC and 15-20 amperes.

Finally, the monitoring site should be fenced and

lighted at night for security reasons. If it is located on residential property, on the roof of a building, or property which is otherwise secure, these requirements may not apply.

Use of Models to Select Monitoring Sites

You can also use atmospheric dispersion models to assist in designing a regional air monitoring program. Modeling results can identify areas of high concentration, relative to actual receptor locations. These high-concentration areas, which correspond to actual receptors, are priority locations for siting air monitoring stations.

However, modeling applications are limited by the amount, quality, and representativeness of the input data. Meteorological data are a key input for developing dispersion or dilution patterns. Unfortunately, the results of standard dispersion models do not accurately represent most complex terrain applications (i.e., the results can be off by greater than a factor of 10). Air dispersion models require emission characterization information as key input. However, the spatial variation of chemical emissions in complex industrial areas may not be well-known. Therefore, modeling may not be appropriate, if adequate input data are not available.

The recommended model to evaluate the dispersion of airborne pollutants for many industrial sources located in areas of flat or gently rolling topography is the Industrial Source Complex (ISC) Dispersion Model.[10] The use of this model is not difficult, and it is available for use on a personal computer. Other approved models, included in the EPA *Guidelines for Air Quality Models*,[7] are also recommended for use, depending on the application under consideration.

If sufficient representative data are available, you can use dispersion modeling to identify the area of maximum, long-term concentration levels at the property boundary and at actual offsite receptor locations. Regional air monitoring stations located at the above locations should provide data to characterize offsite concentrations of airborne pollutants.

Designing a Network for Model Validation

Upwind/downwind ambient air monitoring networks provide concentrations of airborne pollutants at the point of monitoring, relative to the facility or industrial complex under consideration. Each air sample collected is classified as upwind or downwind, based on the wind conditions for the sampling period. By comparing downwind concentrations to those measured at upwind points, you can determine the relative contribution of release from the facility to ambient concentrations of air pollutants. This is generally accomplished by subtracting the upwind concentration (which represents background conditions compared to the facility contribution) from the concurrent downwind concentrations. In many cases, you can directly compare these monitoring results to concentration increments for a specific source, based on dispersion modeling calculations and accurate source emission data.

The locations of air monitoring stations for model validation applications should be based on local wind patterns. Air monitoring stations should be placed at the following strategic locations:

- Upwind of the facility to characterize background air concentration levels (based on the expected prevailing wind flow during the monitoring period).
- Downwind of the facility at offsite receptor locations which are expected to have the greatest impact from the releases, considering prevailing wind flows.
- Additional locations at complex terrain and coastal sites associated with pronounced secondary air flow paths (e.g., downwind of the facility for both primary daytime and nighttime flow paths).

You should select the above locations prior to initial monitoring, based on your evaluation of available representative meteorological data.

3.7 SELECTING CONTRACTORS FOR SAMPLING AND ANALYSIS

This document was designed to present information to develop specifications for obtaining competitive bids from sampling and analysis contractors. You can identify potential contractors from a review of reference documents, open literature, personal experience, and professional contacts. By reviewing contractor literature and publications and by interviewing contractor representatives, you can compile a "short list" of organizations to receive request for proposal on monitoring activities. You may wish to include a questionnaire concerning contractor capabilities in this process. Your request for proposal should specifically describe a scope of work, schedule, deliverables, methods and procedures to be used, and other terms and conditions, so that quotations can be compared on an equal basis. Also, you should advise the potential contractors of any specific requirements for status reports and review meetings, invoicing, and other administrative items. As part of the contractors' response, you should ask them to identify and present the qualifications of any subcontractors that they propose to use for the project. In general, allow three to four weeks to permit bidders to present comprehensive proposals.

You must consider several key factors when evaluating contractor capabilities and quotations for ambient air toxics monitoring. This list is not all inclusive. Develop your evaluation criteria before contractor bids are returned so you have an unbiased yardstick to judge the contractors equitably.

- Experience of assigned personnel on similar projects.

- Educational background and training of assigned personnel.
- Perceived ability of assigned individuals to work harmoniously and effectively with the sponsor's management and field personnel.
- Cost, including rate levels and basis, mark-up percentages, and overtime provisions.
- In-house laboratory capability or established relationship with an outside laboratory.
- QA/QC policy and practices.
- Range of methods employed by the laboratory.
- Mode of communications and management mechanisms between sampling and analytical personnel.
- Flexibility of approach (e.g., availability of leased vs. purchased equipment).
- Contract terms and conditions.
- Proximity and availability of assigned personnel.
- Understanding of the objectives and scope of the program.
- Laboratory certifications.

Following the evaluation of proposals, you may want to conduct further negotiations with one or more bidders. To simplify management of the project, we recommend that one contractor be given overall responsibility for the conduct of sampling and analytical activities, whether or not the laboratory is a part of this organization or is an independent laboratory. (In this latter case, the laboratory would be a subcontractor).

3.8 REFERENCES

1. U.S. EPA, December 1988. *FY-88 Annual Report on the Operations and Findings of the Toxic Air Monitoring Stations (TAMS)* and subsequent updates. Internal Report, Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, North Carolina 27711.

2. Houston Regional Monitoring Corporation, July 1988. *Volatile Indicator Measurement Results from the Houston Regional Monitoring Network* (August 18, 1987 through March 18, 1988) and subsequent updates. Prepared by Radian Corporation, Austin, Texas 78720.

3. U.S. EPA, January 1988. *National Ambient Volatile Organic Compounds (VOCs) Data Base Update* and subsequent updates. EPA 600/3-88/010(A). Contract No. 68-02-4190, prepared by G2 Environmental, Inc.

4. U.S. EPA, May 1987. *The Modified Hazardous Air Pollutant Prioritization System (MHAPPs).* EPA Contract No. 68-02-4330, Work Assignment No. 12, prepared by Radian Corporation.

5. U.S. EPA, August 1988. *Source Category Ranking System.* EPA Contract No. 68-02-4330, Work Assignment 51, prepared by Radian Corporation.

6. U.S. EPA. February 1983. *Quality Assurance Handbook for Air Pollution Measurements Systems: Volume IV, Meteorological Measurements.* EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, North Carolina 27711.

7. U.S. EPA. July 1986. *Guidelines on Air Quality Models (Revised).* EPA-405/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

8. U.S. EPA. May 1987. *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD).* EPA-450/4-87/007. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

9. U.S. EPA. June 1987. *On-Site Meteorological Program Guidance for Regulatory Modeling Applications.* EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

10. U.S. EPA. December 1979. *Industrial Source Complex (ISC) Dispersion Model Users Guide.* EPA Report No. 450/4-79-030. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina 27711.

4.0 OPERATING THE NETWORK

Good operation of the air monitoring network is critical to high-quality data collection and analysis. Therefore, it is imperative that staff assigned to the program be well-trained in various phases of network operation. This will help ensure that the operation and monitoring plan requirements are met.

This chapter discusses of the elements associated with network operations. Figure 4-1 outlines these elements.

Properly trained, in-house personnel involved with the program is an important ingredient for its successful implementation. Section 4.1 provides a discussion on the selection and training of project personnel.

Procuring equipment is also an important element in the program implementation. Section 4.2 provides a discussion of the steps of the procurement process.

Once the equipment is procured, installed, and tested, operating and maintaining the field instrumentation starts. This subject is discussed in Section 4.3.

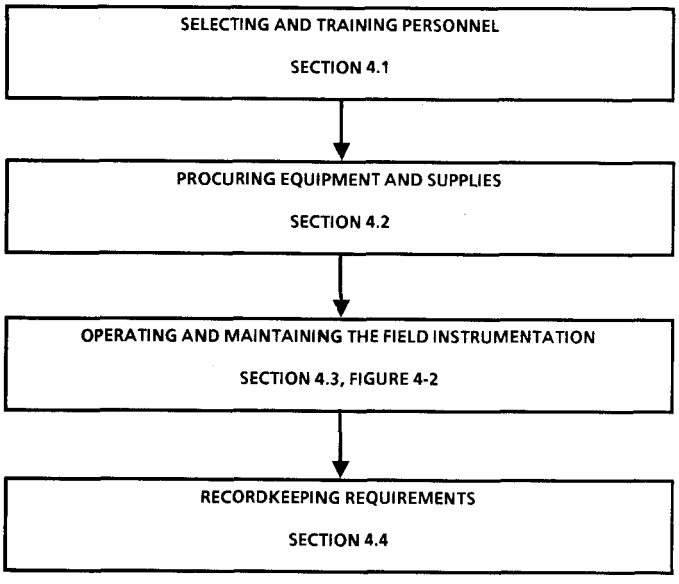
Recordkeeping requirements, including various manuals, logs, information sheets, chain-of-custody forms, and other records, are discussed in Section 4.4.

4.1 SELECTING AND TRAINING PERSONNEL

In-house staff should be involved with regional air monitoring programs at various levels. For example, they may direct and manage the program while implementation is provided by a contractor. Or they may conduct one or more tasks of the program while a contractor performs the remaining tasks.

FIGURE 4-1

KEY ELEMENTS OF NETWORK OPERATION



In any case, all staff involved with the program should thoroughly understand the program's objectives and specific elements. Staff in management roles should have prior experience with regional air monitoring programs. In particular, management personnel should have experience with managing and communicating with contractors, including laboratories; be sensitive to the health risk-perception implications of the resulting air monitoring data; and use skill when relating with agency person-nel, the media, and the general public. Program managers must also maintain a high commitment to developing and implementing quality assurance/quality control programs which meet the needs of their project.

For staff, who may be involved in field activities or other technical roles, prior air monitoring experience is a valuable asset. Their commitment to QA/QC programs is also critical.

Health and safety personnel already may be qualified to participate in the air monitoring operations. However, those unfamiliar with the low detection levels (parts per billion or micrograms per cubic meter), which are typically employed in regional air monitoring, may need training. Therefore, staff involved with field and other technical air toxics monitoring projects should be air quality specialists with relevant ambient air monitoring experience. Regardless of the individuals' backgrounds, they must have a thorough knowledge of, or receive training in, the equipment and methods to be employed. Their familiarity with computerized database management techniques would also be beneficial.

Field personnel in particular must be well-trained in:

- Understanding the operation of the sampling equipment.
- Performing the preventive maintenance actions recommended by the manufacturer.
- Conducting timely equipment checks and calibrations.
- Maintaining the required logs and records to document pertinent field activities. These activities must be clearly documented for future reference.
- Carefully handling collected samples to avoid contamination or loss of materials. This includes documenting, in detail, every sample sent for laboratory analysis to maintain the correct chain-of-custody.
- Carefully maintaining the program schedule for sampling and analysis.
- Carefully checking regenerated equipment (canister, traps, plugs, etc.) that are returned by the laboratory.
- Consistently collecting QA/QC samples.

- Maintaining communications with other project personnel and management to ensure that they are kept apprised of any problems and the means of mitigating them.

An integral part of the network operation is communication with the laboratory selected to analyze field samples. Close communication with the designated contact at the laboratory is critical to ensure that the shipped samples are received and analyzed on time and that any technical issues that develop are handled promptly.

A number of options are available to train project personnel, who need to supplement their prior training and experience. These include reviewing documents developed specifically for this program, such as the program operations plan, and conducting one-on-one meetings with the operations contractor, laboratory contact, or other industry personnel who have conducted regional air monitoring activities. Outside resources, such as U.S. EPA training courses or workshops, are available. Publications, such as the references listed in Section 3.8, are also useful for training purposes. Finally, staff may obtain vendor literature or attend training sessions offered by suppliers of air monitoring instruments.

4.2 PROCURING EQUIPMENT AND SUPPLIES

After a monitoring plan is developed and the program fully designed, procure equipment and supplies.

Procurement involves developing specifications for equipment and supplies and making a list of qualified vendors; evaluating vendors' bids and selecting the successful vendor(s); expediting delivery of equipment and supplies; performing equipment checks, and preparing the equipment for field installation.

Listed below are items that can be used as a basis for developing vendor specifications:

- Type of equipment and basic source requirements.
- Number of pieces necessary for the program.
- List of spare parts.
- List of necessary supplies.
- Equipment instruction manuals and other documentation.
- Warranties.
- Delivery time.
- Equipment calibration and repair services.
- List of clients and number of units sold.
- Equipment costs.
- Reference methods or other third party specifications which must be met.

The bids should be evaluated, based on a selected set of criteria including the following:

- Quality and performance of equipment.
- Supplier performance and track record.
- Delivery schedule.
- Supplier responsiveness.
- Support services.
- Cost.

This evaluation should be made for each piece of air monitoring equipment that is a part of the program, including meteorological equipment. Laboratory and consulting services should also be evaluated.

After you select the successful vendor, order the equipment and make sure it is delivered to the group that will install it.

Before using the equipment, you should check it for proper operation and calibration, if necessary. In addition, it should be inventoried to allow easy tracking. All supplies should be checked and stored at a location convenient for the field operators. Preparation of a good inventory management system ensures a mechanism to replenish supplies on time.

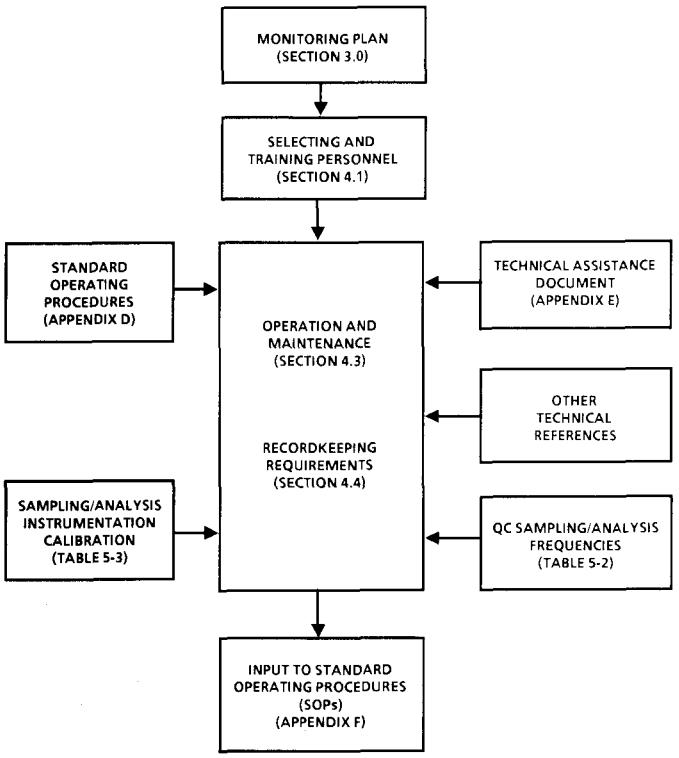
Selecting air monitoring sites and providing access, site security, 110-volt power, lighting, and platforms (if needed) are critical elements of the program that should be completed at the same time as equipment procurement. Typical site preparations include grading, preparing a platform for the instruments, and building a foundation for the meteorological tower.

4.3 OPERATING AND MAINTAINING THE FIELD INSTRUMENTATION

Field and analytical operations of the air monitoring program should be conducted in accordance with the monitoring plan developed for the program (see Chapter 3.0). Successful implementation of the monitoring plan requires adequate field staff, program management, and attention to QA/QC factors. Therefore, program managers should consider applying the operational approach illustrated in Figure 4-2 to regional air monitoring programs. Developing Standard Operating Procedures (SOPs) for each type of air monitoring equipment involved with the program is important. Appendix D includes a bibliography of Air Monitoring Standard Operating Procedures. Appendix E includes an excerpt of QA/QC protocols from the U.S. EPA Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air. Examples of SOPs that are pertinent to regional air monitoring programs are included in Appendix F. These examples cover the operation and maintenance of the canister VOCs sampler and meteorological equipment.

FIGURE 4-2

FIELD INSTRUMENTATION OPERATION AND MAINTENANCE


MONITORING PLAN (SECTION 3.0)
SELECTING AND TRAINING PERSONNEL (SECTION 4.1)
STANDARD OPERATING PROCEDURES (APPENDIX D)
TECHNICAL ASSISTANCE DOCUMENT (APPENDIX E)
OPERATION AND MAINTENANCE (SECTION 4.3)
OTHER TECHNICAL REFERENCES
RECORDKEEPING REQUIREMENTS (SECTION 4.4)
SAMPLING/ANALYSIS INSTRUMENTATION CALIBRATION (TABLE 5-3)
QC SAMPLING/ANALYSIS FREQUENCIES (TABLE 5-2)
INPUT TO STANDARD OPERATING PROCEDURES (SOPs) (APPENDIX F)

The subjects that are addressed in the SOPs generally include, but are not limited to, the following:

- Purpose.
- Applicability.
- Definitions.
- Manufacturers' instructions and specifications.
- Summary of methods, including limitations.
- General requirements for optional operating performance.
- Operating procedures.
- Operating schedule.
- Sample handling (handling in the field, communication issues, packaging and storage, sample tracking [chain of custody], shipment, and other issues).
- Sample holding time.
- Sample analysis.
- Routine equipment calibration and maintenance.
- Program audits.
- Record keeping.
- Program responsibilities.

4.4 RECORDKEEPING REQUIREMENTS

A key factor in a regional air monitoring program is complete, detailed documentation of field and laboratory activities. The required documentation should include the following:

- Personnel Training Records.
- Monitoring Equipment Manuals.
- Monitoring Plan.
- Field Logs.
- Sample Information Sheets.
- Chain-of-Custody Forms.
- Laboratory Logbook
- Sample Analysis Sheets (including support documentation).
- QA/QC Data.
- Audit Checklist.
- Maintenance Records.

Personnel training records for key staff members should be maintained by the group responsible for conducting the air monitoring program.

The Monitoring Plan document should encompass the air monitoring program network configuration and independent station designs. This record should consist of a topographical map showing station locations; a set of drawings, including a site plan with the monitoring locations identified; and a diagram of the sampling equipment for each station. Vendor manuals should also be included in the document.

The field operator should use a Field Log to maintain a record of sample numbers, dates deployed, and sampling conditions. The operator should note equipment condition, sampling problems or equipment failures, observed weather conditions, and unusual site activities in the field log.

The field operator should also complete Sample Information Sheets for each sample. The recorded information should be similar to that required for Field Log Entries. However, the Sample Information Sheets are sample-specific and are considered the primary sample collection documentation. The Field Log is a backup document and presents information on a chronological basis.

A Chain-of-Custody form should travel with each sample from preparation until the analysis is complete. Along with sample identification tags, the Chain-of-Custody form is used as a definitive basis to record each sample's preparation, deployment, and analytical history.

A Laboratory Notebook should also be maintained. This document should contain information regarding

the time and date of sample analysis, as well as notes on the equipment and analytical methods being used. The laboratory should make copies of this notebook and forward it to the appropriate personnel along with the laboratory results.

Laboratory technicians should routinely use Sample Analysis Sheets to document analysis results. These sheets contain a record of detected compounds and amounts for each run, as well as any pertinent information, such as sample recovery rates.

Program staff should develop a standard Audit Checklist to standardize and document quarterly audits (see Section 5.3). The checklist should contain a succinct list of program requirements. It is a useful resource to indicate compliance status.

FIGURE 4-3
TYPICAL CHAIN OF CUSTODY FORM

Sample Number _____

Shipper Name _____

Address _____
Number Street City State Zip

Collector's Name _____ Telephone ( )_____
Signature

Date Sampled _____ Time Sampled _____ Hours _____

Type of Process Producing Waste _____

Field Information _____

_____

_____

Sample Receiver

1. _____
Name and address of organization recieving sample

2. _____

3. _____

Chain of Possessions

1. _____ _____ _____
Signature Title Inclusive Dates

2. _____ _____ _____
Signature Title Inclusive Dates

3. _____ _____ _____
Signature Title Inclusive Dates

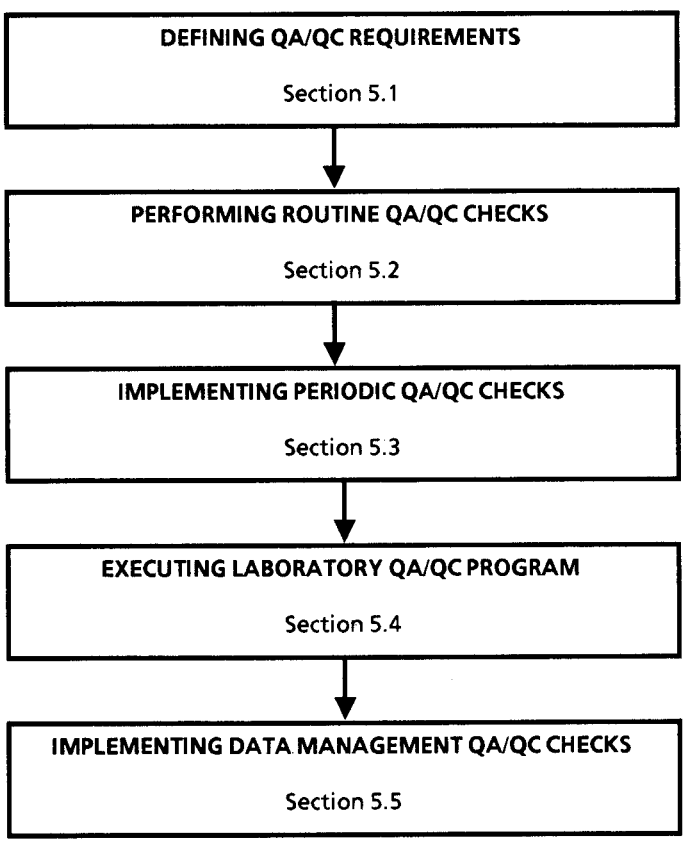
5.0 IMPLEMENTING QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Regional air monitoring programs for airborne pollutants consist of complex activities using monitoring equipment and laboratory analysis techniques. This approach is necessary to accurately quantify concentrations of airborne pollutants in ambient air. Therefore, it is critical that you ensure and maintain a high-quality program, by implementing the appropriate QA/QC program elements.

Figure 5-1 outlines the sections described in this chapter. Section 5.1 provides an overview of the QA/QC elements implemented during the operation phase of the air quality program, Section 5.2 discusses the routine QA/QC checks, and Section 5.3 addresses periodic QA/QC checks. Elements of the laboratory QA/QC program are outlined in Section 5.4. Section 5.5 provides a discussion of data management QA/QC, including the type of validity checks to be performed.

FIGURE 5-1

KEY ELEMENTS OF QA/QC FOR REGIONAL AIR MONITORING PROGRAMS



5.1 DEFINING QUALITY ASSURANCE/ QUALITY CONTROL (QA/QC) REQUIREMENTS

Many people confuse the terms quality assurance and quality control (QA/QC). Both activities are concerned with maintaining consistent and verifiable quality in each element of the program. Strictly speaking, quality control (QC) applies to measures taken, on an ongoing basis, by personnel involved in producing the primary output of the program. These actions are taken to maintain performance parameters within acceptable levels. An example of quality control activity is a routine zero/span calibration check of a monitoring instrument by the responsible operating technician.

Quality assurance, on the other hand, refers to checks or tests performed by personnel, other than the primary operators, to verify that the performance parameters have, in fact, been maintained within acceptable limits. Examples of quality assurance activities are performing a quarterly audit of monitoring instruments and checking output data for "out-of-limits" values. In the discussion which follows, QA/QC is used as a general term to encompass both QA and QC activities.

A rigorous QA/QC effort is necessary during the operation of the regional air monitoring program, to meet monitoring objectives. Major QA/QC elements that you should implement during the operational phase of a regional air monitoring program (see Table 5-1) include QA/QC management, sample QA/QC, analytical QA/QC, and data reduction QA/QC.

QA management involves implementing project-specific administrative procedures to control QA/QC functions. The potential for, and types of, quality problems vary depending on the activity: sampling, analytical, and data reduction. Therefore, the individual QA/QC requirements must be developed for each of these activities. Comprehensive QA/QC recommendations applicable to regional air monitoring programs are available in a number of documents.

Generic air monitoring QA/QC recommendations are included in the *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air.*[1] Monitoring method-specific QA/QC recommendations are covered in documents issued by the U.S. EPA[2,3,4,5] and NIOSH.[6] Air quality monitoring QA/QC recommendations are included in *Quality Assurance Handbook for Air Pollution Measurements*[7] *and Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD).*[8]

TABLE 5-1

QA/QC ACTIVITIES TO BE SPECIFIED IN PROGRAM PLAN

QA/QC Management

- QA/QC System Design
- Document Control
- Data Evaluation
- Audit Procedures
- Corrective Action
- QA/QC Reports to Program Management
- Training

Sample QA/QC

- Instrument Calibration and Maintenance
- Collection of Routine Quality Control Samples
- Data Recording
- Sample Labeling, Preservation, Storage, and Transport
- Chain-of-Custody Procedures

Analytical QA/QC

- Method Validation Requirements
- Instrument Calibration and Maintenance
- Quality Control Sample Analysis
- Data Recording

Data Reduction QA/QC

- Sample and Analysis Data Files
- Storage of Raw and Intermediate Data
- Data Validation

The references are included in Section 5.6. Using the approach illustrated in Table 5-1, you should evaluate these to identify those appropriate for your program-specific QA/QC requirements.

Summaries of typical sampling and analysis frequencies QA/QC requirements, and calibration requirements for sampling and analysis instrumentation are presented in Tables 5-2 and 5-3, respectively.

5.2 PERFORMING ROUTINE QA/QC CHECKS

The regional air monitoring program should incorporate the following four-component approach for routine quality control and assurance checks:

- Use collocated samples for precision checks.
- Use blank samples for accuracy checks.
- Use analytical standards and equipment calibrations for accuracy checks.
- Perform data review for internal consistency.

During each regional air monitoring program, one station with two sets of collocated air samplers should be used in accordance with Section 4.5 siting criteria. The goal should be to obtain at least 10 percent of collocated samples for each monitoring network. The analytical results from the collocated samplers should be used to compare and evaluate the integrity of the samples and the adequacy of laboratory procedures.

Preparation and analysis of sample blanks at some appropriate frequency will ensure program integrity. Ten percent of the total samples collected is considered as a minimum amount for sample blanks. After the sam-

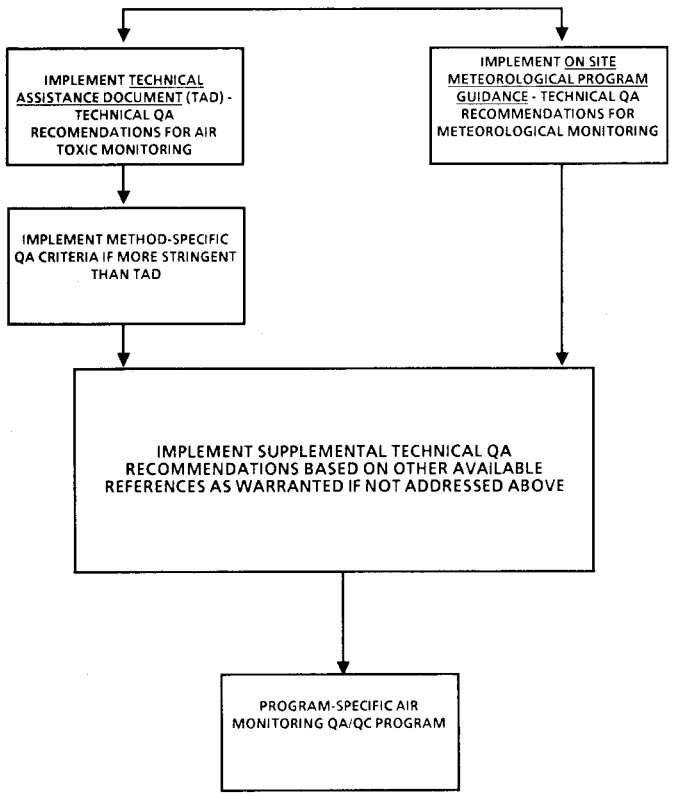
TABLE 5-2

TYPICAL SAMPLING/ANALYSIS FREQUENCIES FOR QC SAMPLES

Type of Sample	Typical Frequency
Field Blanks	Each sample set; at least 10 percent of total number of samples. Not necessary for VOC canisters.
Laboratory Blanks	Daily; at least 10 percent of total number of samples. Each batch of samples.
Spiked Samples	Each sample set; weekly.
Collocated (Parallel) Samples	10 percent of total number of samples.
Instrument Calibration Standards	Daily.
Reference Samples	Weekly.
Series (Backup) Samples	Each sample set.

FIGURE 5-2

REGIONAL AIR MONITORING QA/QC STRATEGY


IMPLEMENT TECHNICAL ASSISTANCE DOCUMENT (TAD) - TECHNICAL QA RECOMENDATIONS FOR AIR TOXIC MONITORING
IMPLEMENT ON SITE METEOROLOGICAL PROGRAM GUIDANCE - TECHNICAL QA RECOMMENDATIONS FOR METEOROLOGICAL MONITORING
IMPLEMENT METHOD-SPECIFIC QA CRITERIA IF MORE STRINGENT THAN TAD
IMPLEMENT SUPPLEMENTAL TECHNICAL QA RECOMMENDATIONS BASED ON OTHER AVAILABLE REFERENCES AS WARRANTED IF NOT ADDRESSED ABOVE
PROGRAM-SPECIFIC AIR MONITORING QA/QC PROGRAM

pling media are prepared for field use, one of each type of medium should be randomly selected as a field blank. They should be deployed in the field, but should not be used to collect ambient samples. Ideally, deploying field blanks should coincide in time and location with the collocated sampling. Analysis of the field blanks for contamination should indicate the acceptability of sample handling and decontamination operations. This procedure is not necessary, for VOC canisters. Canisters must be certified as being clean and free of contamination before sample collection.

Additional routine QA/QC checks are summarized in Tables 5-2 and 5-3.

5.3 IMPLEMENTING PERIODIC QA/QC CHECKS

Periodic QA/QC checks should be implemented to supplement the routine checks. They should include monthly spiked samples, quarterly audits of program performance, and quarterly calibration of measurement and control devices, such as flow controllers, timers, and meteorological equipment.

You can routinely check the accuracy of sample analysis by submitting spiked and blank gas samples, as part of the laboratory analysis package. Spiked samples should contain a known concentration(s) of some of the

TABLE 5-3

CALIBRATION REQUIREMENTS FOR SAMPLING AND ANALYSIS INSTRUMENTATION

Device	Parameter Calibrated	Method of Calibration	Approximate Frequency	Comments
SAMPLING INSTRUMENTATION				
Sampling flow rate measurement device	Flow rate	Wet or dry test meter or appropriate flow rate transfer standard	Depends on sampler (e.g., weekly, monthly, etc.)	
Sample volume measurement device (usually a dry test meter)	Total volume	Wet test meter or any appropriate volume standard.	Depends on sampler (e.g., weekly, monthly, etc.)	Must be determined at known atmospheric pressure and temperature. Flow rate should be similar to that used for sampling.
ANALYTICAL INSTRUMENTS				
Continuous monitors (e.g., FID, PID, FPD, etc.)	Response	Use standard concentrations	Daily or more frequently, if required	Test atmosphere should be referenced to a primary standard (e.g., NIST, SRM, or CRM*). Flow/pressure conditions should duplicate sampling process.
Chromatographic instruments	Column performance and response retention time for each analyte	Injection of standard using the same process as for sample injection	Daily or more frequently if required	Standard composition should be checked against primary standards if available.
GC/MS	Response and retention time for each analyte	Same as for other chromatographic instruments	Same as for other chromatographic instruments	Same as for other chromatographic instruments.
GC/MS	Mass spectral resolution and tuning parameters	(a) Introduction of perfluoro-compound directly into MS (b) Injection of tuning standard (e.g., bromofluoro-benzene) into GC	Daily	Selection of tuning standards will be dependent on type of analysis being performed.

* NIST - National Institute Standardization Technology,
SRM - Standard Reference Material,
CRM - Certified Reference Material

same compounds that the laboratory is performing analysis. Blank samples contain only inert compounds (e.g., nitrogen).

In addition, a quarterly onsite audit is recommended for the air monitoring program. The audit should consist of the following:

- Inspecting sampling stations for general physical condition and operability.
- Re-evaluating the source activities.
- Evaluating the technical performance and record-keeping procedures. These are compared to the specifications in the monitoring plan and appropriate Standard Operating Procedures.
- Auditing the air monitoring equipment.
- Auditing the meteorological equipment.

Additional routine QC checks are summarized in Tables 5-2 and 5-3.

5.4 EXECUTING LABORATORY QA/QC PROGRAM

Laboratory analytical techniques must properly identify the sample components and accurately and precisely measure concentrations. This generally requires the preconcentration and/or storage of air samples. Therefore, methods chosen for time-integrated monitoring usually involve a longer analytical time period, more sophisticated equipment, and more rigorous QA procedures. Canister sampling includes replicate analyses and duplicate canisters to assess analytical and sampling precision. Exchanging samples with other laboratories is desirable to check analytical performance.

Laboratory QC methods for the regional air monitoring project should include the following elements: replicates, spiked samples, control charts, blanks, canisters certification and cleanup, internal standards, zero and span gases, quality control samples, surrogate samples, calibration standards and devices, and reagent checks.

The laboratory performance in implementing these elements should be considered as a part of the laboratory selection process. Specifications for implementation of these laboratory QC checks are summarized in Tables 5-2 and 5-3. In addition, the analytical methods selected for program application generally include specific laboratory QA/QC checks.

5.5 IMPLEMENTING DATA MANAGEMENT QA/QC CHECKS

Raw monitoring data should be checked for validity, before they are used as a part of the data base for site decision-making. These validity checks are an integral part of the QA/QC program for monitoring activities. A qualified person, who is not directly involved with the laboratory activities, should validate the data. Elements of the data validation include evaluation of the quality of the raw monitoring data against the field and laboratory QA/QC data and verification of the calculations of ambient concentrations.

Meteorological Data Validation

The validity of raw meteorological data should be checked using equipment calibration, audit, and performance data. Comprehensive technical recommendations for meteorological data validation are presented in *On-Site Meteorological Program Guidance for Regulatory Modeling Applications.*[5] A summary of applicable meteorological data screening criteria is presented in Appendix G.

Air Monitoring Data Validation

Similarly, the validity of air monitoring data should use equipment calibration, audit, and performance data in a manner similar to that recommended for meteorological data.

A qualified chemist, who is familiar with both the data validation requirements and the process, should validate the analytical results. Validation of analytical results for one sample could take from 15 minutes to more than an hour, depending on the type of analysis used, the number of air toxic constituents involved, interference, contamination, and other factors.

Raw air quality data received from portable GC analyzers or other continuous instruments must be checked for validity. The performance of the analyzer, calibration information, and QA results should be considered.

Air monitoring data validation efforts should include statistical analysis, considering collocated sample results and audit results, to determine data precision and accuracy. A recommended statistical procedure is presented in Appendix G.

5.6 REFERENCES

1. U.S. EPA. June 1983. *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air* and subsequent updates. EPA-600/4-83-027. NTIS PB83-239020. Office of Research and Development. Research Triangle Park, North Carolina 27711.

2. U.S. EPA. April 1984. *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* and subsequent updates. EPA-600/4-87-006. NTIS PB87-168696. Office of Research and Development. Research Triangle Park, North Carolina 27711.

3. U.S. EPA. September 1986. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* and subsequent updates. EPA-600/4-87/006. NTIS BB87-168696. Office of Research and Development. Research Triangle Park, North Carolina 27711.

4. U.S. EPA. June 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* Second Supplement, (TO-10 through TO-14), and subsequent updates. EPA Revision 6/88. Office of Research and Development. Research Triangle Park, North Carolina 27711.

5. U.S. EPA. June 1987. *On-Site Meteorological Program Guidance for Regulatory Modeling Applications.* EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

6. NIOSH. February 1984. *NIOSH Manual of Analytical Methods.* NTIS PB85-179018. National Institute of Occupational Safety and Health. Cincinnati, Ohio 45226.

7. U.S. EPA. February 1983. *Quality Assurance Handbook for Air Pollution Measurements.* EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, North Carolina 27711.

8. U.S. EPA. May 1987. *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD).* EPA-450/4-87-007. NTIS PB81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

6.0 MANAGING AND EVALUATING THE DATA

Obtaining and evaluating data from your regional air monitoring program is your key objective. Steps to handle, process, and report data are discussed in this section.

Section 6.1 provides guidance to store and summarize meteorological and air quality data, including the type of summaries recommended. The format of the database, however, is not provided in this document. Currently, CMA is in the process of developing a consistent format for regional air monitoring data.

After your data is summarized, the interpretation process starts. Section 6.2 discusses how to interpret the results. Section 6.3 addresses the steps associated with re-evaluation of program progress.

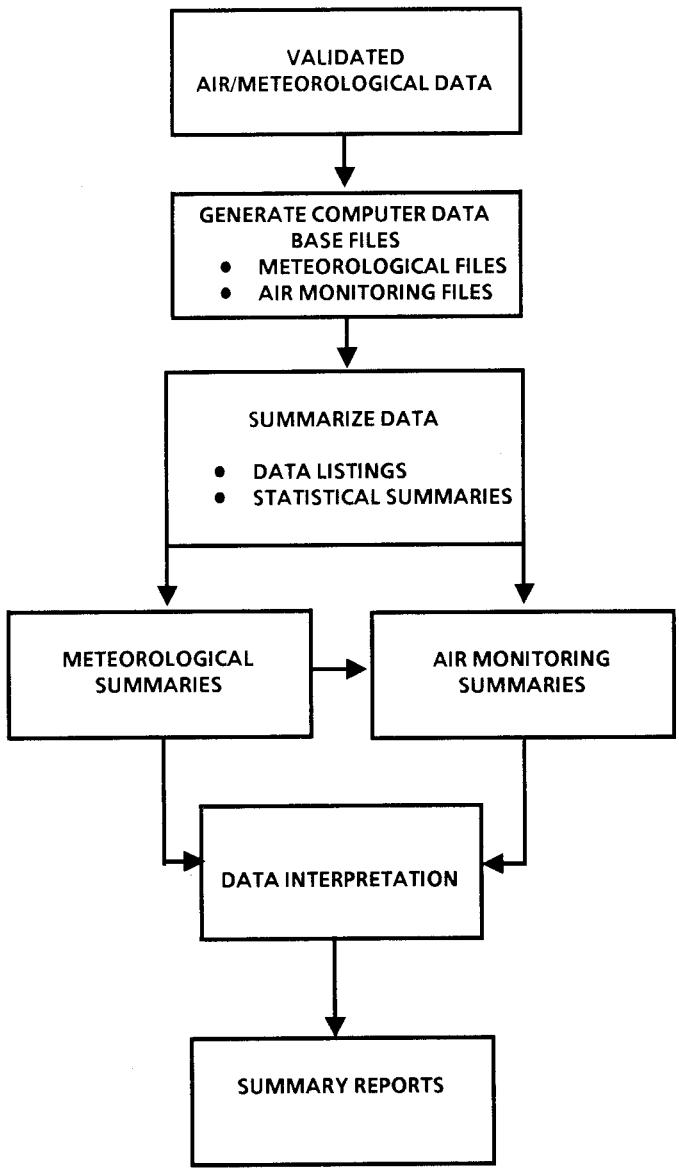
6.1 STORING AND SUMMARIZING THE DATA

The recommended process for managing and evaluating data from a regional air monitoring program is summarized in Figure 6-1.

The first step in the process of summarizing and evaluating the data includes developing a way to handle the data, usually using a computerized data base. Each meteorological monitoring station should be equipped with an automated data processor that provides hourly average values for each parameter. These data should be in a digital format that is directly computer-compatible. Air sampling information and results need to be transcribed from hardcopy records to computer files.

Monitoring data summaries should be prepared, using the validated data bases as input. By using these meteorological and air monitoring data summaries, program managers can readily identify airborne concentrations at various locations. The main reason to perform regional air monitoring is to collect high-quality, credible data. Therefore, data from air monitoring and meteorological stations must meet data recovery requirements. Currently, for permitting purposes, EPA requires data recovery rates (total number of valid observations divided by the total number of possible observations) of 80 percent for air quality data and 90 percent for meteorological data. Any regional air monitoring system established should plan to meet or exceed these requirements to ensure credibility of the results.

FIGURE 6-1
SUMMARIZE AND EVALUATE RESULTS



Meteorological Data Summaries

Meteorological data summaries should include at the least the following:

- Listing of hourly averages of all meteorological parameters for the air sampling periods. This includes average wind speed, wind direction, wind vector, ambient temperature, and atmospheric stability. Recommended units are miles per hour (mph) for wind speed, degrees relative to north for wind direction (with this designation indicating the direction from which the wind is blowing), and ambient temperatures in °F.

- Summary wind roses including daytime and nighttime wind roses for complex terrain sites and those located near large water bodies.
- Tabular summaries of means and extremes for temperature and other meteorological parameters.
- Data recovery summaries for all parameters (stating percent recovery).

Generally, meteorological listings should generally be presented on a sequential hourly basis. A 1-hour time frame is sufficient to account for any short-term temporal variability of the data. The presentation of data for periods less than 1 hour long unduly complicate the data evaluation process. In addition, these shorter-term listings would be voluminous. For those cases where multiple meteorological stations are used at a single network, it is desirable to list the data in adjacent columns to facilitate meteorological data comparisons.

Statistical summaries for the meteorological data should be calculated monthly, seasonally, annually, and for the entire monitoring period.

For sites with diurnal wind patterns (e.g., at complex terrain or coastal areas), separate wind roses should be prepared to characterize daytime conditions and nighttime conditions. A summary wind rose (based on all wind observations during the monitoring period) should also be developed. A suggested format for wind rose data is illustrated in Figure 6-2.

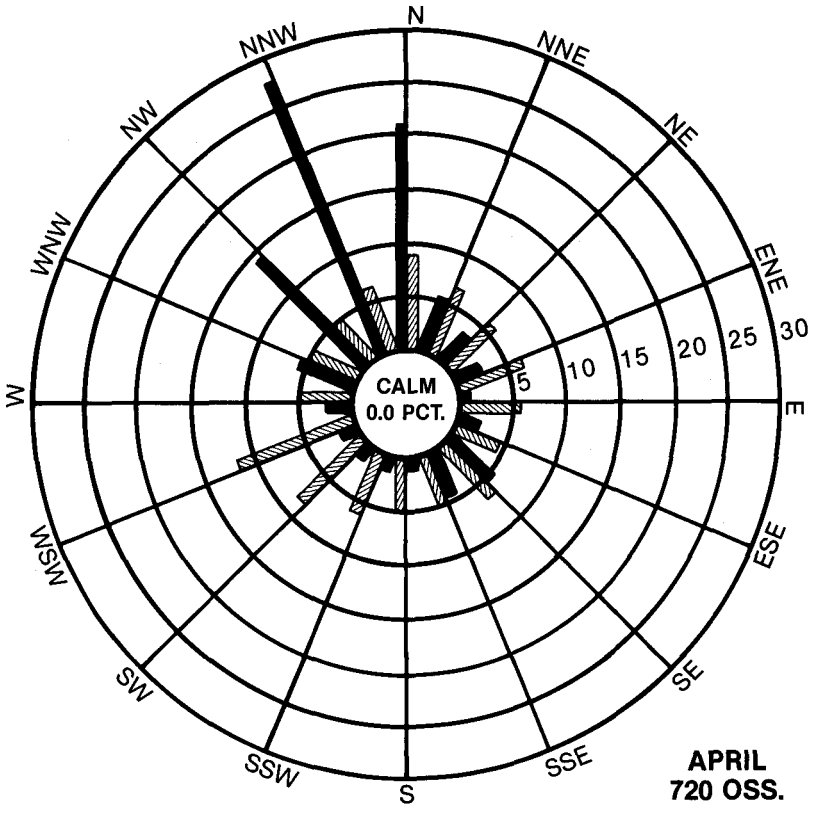
Data recovery (of a portion of acceptable data out of the total database) information should also be presented to allow for an evaluation of data representativeness. As mentioned above, EPA currently requires, for permitting purposes, a minimum meteorological data recovery target of 90 percent.

Air Monitoring Data Summaries

Air monitoring data summaries should include a listing of sequential concentrations, measured by station and monitoring period, that indicates concentrations of all constituents for which monitoring was conducted. The listing should indicate method detection limits for those cases where a constituent is not detected, as well as upwind/downwind exposure classification (when applicable) and monitoring station operation data (e.g., sampling flow rates, station number, and sampling start/end times).

FIGURE 6-2

EXAMPLE WIND ROSE FORMAT



It is recommended that you report a concentration of a constituent that is below method detection limit as ND (not detected) and to use half the detection limit value for statistical calculations. This procedure is often done in the technical community. For example, if the detection limit for benzene is 1 part per billion (ppb) and laboratory analysis indicates concentrations below method detection limit, then the value will reported as ND (1.0 ppb). However, for statistical calculations, a value of 0.5 ppb will be used. If more than 30 percent of the values are below the detection limit, no statistical calculations should be attempted.

Air concentrations should be expressed in μ g/m3 or ppb. Raw data used to derive the concentration are also useful to list in supplemental tables. Such data would include sampling start and end times, constituent content in the sample in μ g, volume of air sampled over the sampling period in m3, and temperature and pressure conditions during sampling time in °F and mm Hg, respectively.

Summary tables of constituent-specific concentrations measured for each monitoring station should include the following: minimum and maximum concentrations; QA/QC concentrations including blanks, duplicates, and others; detection limits; frequency above and below detection limits; number of samples; number of occurrences of air concentrations exceeding selected values (e.g., health and safety criteria, and odor thresholds); and, when applicable, upwind/downwind concentration summaries.

A narrative discussion of sampling results should indicate the problems encountered; the relationship of the sampling activity to unit operating conditions and meteorological conditions; sampling periods and times; background levels and other air emission sources; and interferences that may complicate data interpretation. Also include data recovery for all parameters.

Statistical summaries of air monitoring data should be presented monthly, seasonally, as well as annually, and for the entire monitoring period. In addition to concentration, means, and extremes, these summaries should present any other information useful for interpretation, especially if monitoring results are below analytical detection limits.

Also, present data recovery information to evaluate data representativeness. A minimum data recovery target should be 80 percent.

6.2 INTERPRETING THE RESULTS

When interpreting the results of the program, the air monitoring data should be compared to some constituent-specific health criteria, applicable state/local air toxics guideline, or ambient air standards. It is important that the monitoring results be compared to the appropriate health-based criteria. For instance, the maximum observed values, if collected over a one hour period or less should be compared only to acute health based criteria, such as an EEGL (Emergency Exposure Guideline Limits) or IDLH (Immediately Dangerous to Life and Health) or some short-term criteria. Conversely if potential oncogenic hazard is being evaluated, the average air value should be the basis for comparison. This average should include "not detected" values at some fraction of the detection limit (e.g., detection limit/2 if the majority of values are detected). In no case should a significant risk be inferred from values that are not detected; for example, by using the detection limit for not detected values, then inferring a significant risk at the detection limit, but from values which are not detected. It is recommended that the Constituent Ranking Index (CRI) approach discussed in Section 3.2 and Appendix B can be used for this comparison. The CRI value can be considered as the ratio of the air concentration (based on monitoring results) to the appropriate health criterion. If any calculated CRI exceeds unity (i.e., 1), then additional evaluation or assessment is needed to determine whether a health criterion is exceeded. CMA, under another project, published a companion resource document to aid in this evaluation. This document is entitled, "Chemicals in the Community: Methods to Evaluate Airborne Chemical Levels."[2] Copies of this book are available from CMA publication fulfillment by asking for "Community Exposure Evaluation" booklet.

Monitoring results can also be used as direct input to standard risk assessment models. This alternative data interpretation approach can be used to quantify the total population risk and maximum individual risk associated with ambient concentrations of airborne pollutants.

6.3 RE-EVALUATING THE PROGRAM

The regional air monitoring program should be re-evaluated quarterly. The program review should focus on determining whether program objectives are being attained. Specifically, among the factors that should be evaluated during the initial program review and quarterly, thereafter are the following:

- Program accomplishments versus objectives.
- Adequacy of data quality.
- Adequacy of detection levels.
- Occurrence of sample contamination.
- Sample matrix interference problems.
- Acceptable data recovery.
- Performance of personnel and equipment.

In addition, subsequent annual program reviews should consider the following factors:

- Representativeness of data to characterize typical,

long-term and worst-case, short-term air toxics conditions in the region.

- Changes in population distribution.
- Changes in the type or amounts of airborne pollutants released in your region.
- Changes in needs of the program sponsors.
- Cost-effectiveness of the program.
- Changes in public perception of regional air airborne concentrations and/or potential exposure opportunities.
- Emerging regulatory issues.
- Availability of improved sampling/analytical methods and equipment.

Based on the above factors, you can determine whether program modifications are needed or whether the monitoring should be discontinued.

6.4 REPORTING RESULTS AND CONCLUSIONS

Generally, the public and media are interested in obtaining results from regional air monitoring programs. Therefore, consider presenting these results during a meeting with representatives from these audiences. During these meetings, it is imperative to communicate effectively. CMA, in collaboration with risk communication experts, prepared a resource document entitled, *Risk Communication, Risk Statistics, and Risk Comparisons (CMA, 1988).*[3] For your use, the basic CMA communication strategy includes the following rules:

- Accept and involve the public as a legitimate partner.
- Plan carefully and evaluate your performance.
- Listen to your audience.
- Be honest, frank, and open to ideas.
- Coordinate and collaborate with other credible sources.
- Meet the needs of the media.
- Speak clearly and with compassion.

When writing a summary report for the regional air monitoring program, consider including the following topics:

- Introduction and objectives
- Executive summary
- Monitoring program operations
- Network configuration
  - Meteorological monitoring
  - Air sample collection and analysis
- Monitoring results
  - Meteorological conditions
  - Air sampling results
  - Quality control
- Data interpretation
  - Meteorological conditions and representativeness
  - Air concentrations vs. health/environmental criteria
  - Program performance (QC and audit results)

The report should provide sufficient details about the methodologies employed in sample collection and analysis, data management, and QA/QC procedures. Data summaries should include the type of information discussed under Section 6.1. The availability of raw data that can be used to arrive at the calculated air concentrations, as discussed in Section 6.1, is critical. Sponsors of the program should agree on ground rules for making the raw data available to outside parties.

Data should be interpreted, based on the discussion in Section 6.3. Emphasis should be placed on relating sources to receptors, by using wind direction data associated with measured concentrations. In addition, risk assessment calculations should be performed at least within the framework outlined in Appendix B. Other methodologies can be used, depending on the applications involved and the quality of the experimental animal data.

Volume of data does not result in better interpretation. Instead, valid interpretations require high-quality data that is representative of the ambient concentrations in the region. Hence, in the summary report, it is important that you provide detailed clearly-stated assumptions or qualifications related to data interpretation.

6.5 OPTIONAL USE OF RESULTS IN MODEL VALIDATION

Model validation is not easy. However, results of ambient air measurements can be used to validate models, provided that the design for the monitoring program includes considerations for such validation. Section 3.6 discusses key program design factors to ensure adequate data quantity and quality for model validation. These factors include (1) the number of monitoring stations considering the topography or nearby large water bodies; (2) the location of upwind and downwind stations; (3) sampling frequency and duration; (4) number of samples to be collected; and (5) the quality of sampling and meteorological data, including accuracy and precision.

Model validation requires the identification of a candidate model and the development of a reasonable emission inventory. Then monitoring data can be used in model validation. The American Meteorological Society's 1981 document entitled, *"Air Quality Modeling and the Clean Air Act"*[4] provides a variety of steps

that can be used as a measure of the model performance. These include:

- The bias (average) of the difference (observed minus predicted values)
- The variance of the difference (noise).
- The gross variability (gross error) of the difference.

In addition, measures of correlations can be performed in time, space, or both. Details of the methodologies are outlined in documents produced by the American Meteorological Society[4] and the U.S. EPA.[5]

In certain cases, model validation for industrial sources emitting toxic chemicals can be difficult. This is because many of the dispersion models currently used are not capable of handling reactive, volatile organic compound emissions in the atmosphere. Furthermore, quantifying the air emissions of the specific pollutant, a critical input to the dispersion model, can be difficult. Such factors should be considered as a part of the design of a model validation program.

6.6 REFERENCES

1. U.S. EPA, 1978. *Guidelines on Air Quality Models (Revised).* EPA-405/2-78-027R. NTIS PB86-245248. Office of Air Quality Planing and Standards. Research Triangle Park, North Carolina 27711.

2. Chemical Manufacturers Association, 1988. *Chemicals in the Community: Methods to Evaluate Airborne Chemical Levels.* Washington, D.C. 20037.

3. Chemical Manufacturers Association, 1988. *Risk Communication, Risk Statistics, and Risk Comparisons: A Manual for Plant Managers,* Washington, D.C. 20037.

4. American Meteorological Society, 1981. *Air Quality Modeling and the Clean Air Act.* Recommendations to EPA on Dispersion Modeling for Regulatory Applications, Boston, Massachusetts.

5. U.S. EPA. October 1979. *Procedures for Evaluating the Performance of Air Quality Simulation Models.* EPA-450/4-79-033. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina 27711.

7.0 ESTIMATING PROGRAM COSTS

One of the key questions you will ask is, "How much does it cost to implement a regional air monitoring program?" This chapter provides both unit costs and overall estimated costs for two scenarios of regional air monitoring programs. Cost estimates in this chapter should serve as a guidance for budgetary purposes only. These estimates (July 1989) are based on conversations with equipment manufacturers, suppliers, analytical laboratories, contractors, and/or the author's experience implementing various phases of air monitoring programs. Program costs will vary across the country, depending on the availability of equipment manufacturers and suppliers, analytical laboratories, and contractors. Program managers should get firm quotes to identify the costs specific to your regional air monitoring program needs.

Section 7.1 discusses the unit costs for air quality and meteorological monitoring equipment and supplies as well as for laboratory analysis. Section 7.2 provides cost estimates for two program scenarios: one for a 90-day survey and one for a 1-year study.

7.1 UNIT COSTS OF EQUIPMENT, SUPPLIES, AND ANALYSES

Cost estimates for equipment, supplies, and laboratory analyses for regional air monitoring programs are included in Table 7-1. Key assumptions made in developing these estimates are provided as notes to this table. Monitoring equipment is divided into three groups: time-integrated air monitoring equipment, near-real-time air monitoring equipment, and meteorological monitoring equipment. The equipment selected for inclusion in Table 7-1 is based on the sampling and analysis methods discussed in Section 3.5 and Appendix C. When applicable, the EPA-designated sampling and analysis method is listed in this table.

Two types of equipment and supply costs are provided in Table 7-1. One is for purchasing and the other is for equipment leasing. The leasing cost is based on recovering the purchase price over a period of 1 year. Table 7-1 also includes cost estimates for laboratory analysis.

Additional assumptions that were made in developing the costs presented in Table 7-1 are:

- The cost of a canister sampler includes three canisters, at total cost of $1,350 to $1,500. Three canisters are included with each sampler to ensure continuity of the sampling program, while the analysis is performed.
- The cost of sorption tube samplers (Tenax® and carbon molecular sieve) includes 30 tubes, at a total cost of $1,000.00 to $1,500.00.
- The cost of the Tedlar® bag sampler includes a supply of 30 bags at a total cost between $800.00 to $950.00.
- The cost of a polyurethane foam (PUF) sampler includes brushes, 60 PUF plugs, and 100 fiberglass filters at a total cost of $300 to $500. Each PUF calibration kit costs between $100 to $400. When more than one monitoring station is considered for the network, only one calibration kit should be purchased. Hence, a cost adjustment should be made to exclude this cost of having more than one calibration kit.
- The cost of the high-volume PM-10 sampler includes brushes and 100 quartz filters at a total cost of $500 to $700. A PM-10 calibration kit costs between $100 to $350. As mentioned above, when more than one sampler is purchased, cost adjustment should be made to exclude the cost of more than one calibration kit.

7.2 PROGRAM SCENARIO COSTS

Two cases were developed as examples for program cost scenarios. These can guide the development of other cost scenarios. However, it should be emphasized that the cost estimates developed can be used only for budgetary and planning purposes. Refinements should be made, based on written quotes from equipment manufacturers and suppliers, analytical laboratories, and contractors.

Case I: Short Duration Survey

In this example, the objective for this short duration survey is to monitor VOCs in a region that includes several large industrial facilities. This survey could stand alone or serve as Phase I of a two-phase program. In the case where the short duration survey is Phase I of a larger program, the survey purpose is to collect data at several locations within the community during a season where meteorological conditions are conducive to high ground-level concentrations of air pollutants. Then, this survey will serve as a basis for a long-term monitoring study.

The survey study is scheduled to occur over a 90-day period. Two sampling systems are planned with an additional system as a collocated unit. In the middle of the program, the two sampling stations will be relocated. This way, data are collected from four sites. The resulting data will be used to provide a preliminary assessment of the industrial source contributions to ambient air quality within the region.

TABLE 7-1

RANGES OF UNIT COST ESTIMATES FOR EQUIPMENT AND SUPPLIES AND LABORATORY ANALYSIS FOR REGIONAL AIR MONITORING PROGRAMS

Monitoring	EPA Sampling and Analysis Method[6]	Cost		
		Equipment and Supplies[7]		Laboratory Analysis[8] ($/Sample)
		Purchasing ($/Unit)	Leasing ($/Unit/Month)	
TIME-INTEGRATED AIR MONITORING				
VOC Gas Phase				
• Canister sampler[1]	TO-14	5,400 - 7,500	450 - 650	450 - 500[9]
• Tenax sampler[3]	TO-1	4,000 - 5,000	350 - 450	300 - 350[11]
• Tedlar bag sampler[2]	Modified TO-3 or TO-14	3,800 - 4,500	350 - 400	300 - 350[10]
• Carbon molecular sieve sampler[3]	TO-2	4,000 - 5,000	350 - 450	300 - 350[12]
PCB Particulate				
• PUF sampler[4]	TO-4	2,800 - 3,400	250 - 300	250 - 300[13]
Metals Particulate				
• High-Volume PM-10 sampler[5]	40 CFR Part 50.11 Appendix B	4,500 - 5,200	400 - 450	200 - 250[14]
NEAR-REAL-TIME AIR MONITORING				
VOC Gas Phase[15]	Not available	16,000 - 20,000	1,500 - 1,700	Not applicable
METEOROLOGICAL MONITORING				
Portable system on a tripod with a chart recorder	See Note 19	3,800 - 6,400[16]	300 - 400[17]	Not applicable
Portable system on a tripod with data logger	See Note 19	7,300 - 10,400[18]	600 - 750[17]	Not applicable
Cranked up 10-meter tower system with a chart recorder	See Note 19	4,500 - 7,300[16]	Assumed no lease	Not applicable
Cranked up 10-meter tower system with data logger	See Note 19	8,000 - 11,300[18]	Assumed no lease	Not applicable

(1) Includes 3 canisters.
(2) Includes 30 bags.
(3) Includes 30 tubes.
(4) Includes 30 plugs and 100 fiber glass filters.
(5) Includes 100 quartz filters.
(6) See Appendix C for more details.
(7) Price range is for one unit. Discounts are available for volume purchasing.
(8) Price range is for one sample. Discounts are available for volume analysis.
(9) Method TO-14 analysis, detection limit of about 1ppb and canister regeneration.
(10) Method TO-3 or TO-14 analysis, detection limit of about 1ppb.
(11) Method TO-1 analysis, detection limit of about 1ppb and tube regeneration.
(12) Method TO-2 analysis, detection limit of about 1ppb and tube regeneration.
(13) Method TO-4 analysis, detection limit of about 1-2$\mu g/m^3$.
(14) Atomic absorption/Inductive Coupled Plasma analysis, detection limit of about 1-2$\mu g/m^3$.
(15) Includes portable field GC systems.
(16) System includes wind speed, wind direction, sigma theta and ambient temperature sensors, lightning protection, spare parts, and calibration kits (upper-range cost).
(17) Cost is based on system described under Note (16) without calibration kits.
(18) Also includes chart recorder as a backup to the data logger.
(19) Meets requirements specified in Reference 8 in Section 5.6 (EPA-450-/4-87/007) and Reference 5 in Section 5.6 (EPA-450/4-87-013).

The following assumptions apply to this cost example:

- Two air monitoring equipment options could be used: (1) time-integrated VOCs monitoring using whole air canister samplers, with subsequent laboratory analysis or (2) near-real-time portable field GC analyzers.
- The survey will include a portable meteorological station.
- The survey will be conducted for a period of 90 days using two sampling systems with an additional collocated system (for a total of three systems). The samplers will be moved mid-program, so that a total of four sampling locations are used.
- The monitoring equipment will be leased during the 90-day study.
- Samples will be collected over a period of 24 hours on every third day.
- Fifteen samples will be collected at each of the four sampling locations for a total of 60 samples.
- QA/QC samples for the first option will include 25 samples collected over the 90-day period by the collocated samplers.
- QA/QC samples for the second option will include 15 canister samples.
- Site preparation costs (e.g., for electric power and fencing) are not included.

Table 7-2 provides the cost estimates for a short duration VOCs monitoring survey. The range of estimated costs for Option 1 (three time-integrated, whole-air

TABLE 7-2

EXAMPLE RANGE OF COST ESTIMATES FOR IMPLEMENTING THE CASE I SHORT-TERM VOCs AIR MONITORING SURVEY

	Cost Elements	Cost ($)*
Capital Cost	VOCs Air Monitoring	
	• Option 1:3 Time-integrated whole-air canister samplers	4,500 - 6,000
	• Option 2:3 Near-real-time portable field GC analyzers	13,500 - 15,500
	Meteorological Monitoring	
	• One portable system on a tripod with a chart recorder or a data logger	1,000 - 2,500
	Spare Parts	500 - 1,000
	Platforms/Instrument Shelters - three units	1,500 - 2,000
Startup Cost	• Develop monitoring plan	
	• Lease equipment and initial check-out	21,500 - 27,500
	• Set up equipment in the field	
	• Train in-house personnel	
Operation Cost	• Option 1 (three time-integrated, whole-air canister samplers)	
	- Supplies and samples shipment	3,500 - 4,000
	- Laboratory analysis	38,500 - 42,500
	- One audit	4,000 - 5,000
	• Option 2 (three near-real-time portable GC analyzers)	
	- Supplies and samples shipment	500 - 1,000
	- Calibration supplies and other expendables	3,000 - 5,000
	- Laboratory analysis	7,000 - 7,500
Data Management and Reporting	• Data validation	2,000 - 2,500
	• Processing meteorological data	1,500 - 3,500
	• Processing air quality data	2,000 - 3,500
	• Interpretation and reporting	4,500 - 6,500
Total Cost	• Option 1 Monitoring	84,500 - 106,500
	• Option 2 Monitoring	58,500 - 78,000

*Numbers are rounded to the nearest $500.

canister samplers) is $84,500 to $106,500. The range of estimated costs for Option 2 (three near-real-time portable field GC analyzers) is $58,500 to $78,000. The main difference between the two options can be attributed to the large laboratory analysis cost under Option 1. However, using the second option could mean less accurate results, because of some of the limitations of portable field GC analyzers. You should weigh these factors when selecting one of the two options.

Case II: Long-Term Study

In this example, the purpose is to establish a long-term regional air monitoring program to measure both VOCs and metals in a region with several large industrial facilities. The objective of this study is to establish ambient levels of VOCs and metals at several locations within the community over a period of a year or more. The data obtained will be used to evaluate the VOCs and metals concentrations contributed by the industrial facilities.

The monitoring program will include three fixed monitoring stations. Each will inlcude a VOCs sampler and a high-volume PM-10 sampler to collect particulate matter samples for metals analysis. One of the sites will include a meteorological station and additional collocated VOCs and PM-10 samplers.

The following assumptions apply to this cost example:

- The network will include three fixed stations.
- The network will operate for one year.
- The network will include four, time-integrated, whole-air canister samplers; four time-integrated, high-volume PM-10 metals samplers; one 10-meter meteorological station; and auxiliary equipment and supplies.
- The meteorological station will consist of wind speed, wind direction, sigma theta, and ambient temperature sensors mounted on a crank-up 10-m

TABLE 7-3

EXAMPLE RANGE OF COST ESTIMATES FOR IMPLEMENTING CASE II LONG-TERM REGIONAL AIR MONITORING PROGRAM FOR VOCs AND METAL PARTICULATE

	Cost Elements	Cost ($)
Capital Cost	VOC Air Monitoring	
	• 4 Time-integrated, whole-air canister samplers	22,000 - 30,000
	Metals Air Monitoring	
	• 4 Time-integrated, high-volume PM-10 samplers	17,000 - 18,000
	Meteorological Monitoring	
	• One fixed system mounted on a 10-m cranked up tower with a data logger system	8,000 - 11,500
	Spare Parts	1,000 - 2,000
	Platforms/Instrument Shelters - three units	2,000 - 2,500
Startup Cost	• Develop monitoring plan	
	• Procure equipment and initial check-out	26,000 - 41,000
	• Install equipment in the field	
	• Train in-house personnel	
Operation Cost	• Supplies and samples shipment	11,500 - 12,500
	• Laboratory analysis for 232 canister samples and 266 filter samples	173,000 - 199,500
	• Four quarterly audits	16,000 - 20,000
Data Management and Reporting	• Data validation	6,500 - 9,000
	• Processing meteorological data	6,000 - 8,500
	• Processing air quality data	8,000 - 13,000
	• Interpretation and reporting	16,000 - 23,500
Total after the first year		271,100 - 360,400

tower; supporting electronics; data logger; and a chart recorder.

- Air samples will be collected once every sixth day at the three sites for a total of 198 VOCs canister samples and 198 filter samples.
- QA/QC samples will include 34 samples collected at the collocated VOCs and particulate metal samplers, add 17 field blanks, and 17 trip blank samples for particulate metals only. This results in a total of 68 VOC canister samples and 34 filter samples.
- The monitoring plan will include a detailed air dispersion modeling study (reflected in the upper range startup cost).
- No adjustment was made to the cost to account for discounts on the large volumes of samples to be analyzed. A cost adjustment could be 10 to 20 percent, depending on the arrangements made with the laboratory.
- Site preparation costs (e.g., for electrical power, and fencing) are not included.

Table 7-3 provides the cost estimates for a long-term regional air monitoring study measuring VOCs and metals particulates. These cost estimates do not include the short duration survey. If you choose to adopt a two-phase program, a short duration survey, and then a long-term fixed monitoring study, the costs must be adjusted to avoid double counting expenses. In particular, adjustments will be needed for capital and startup costs.

Capital costs range from $50,000 to $64,000 dollars. Startup costs range from $26,000 to $41,000. Estimated annual operating costs as well as data management and reporting costs range from $237,000 to $286,000. This results in an estimated first-year total cost range of $313,000 to $391,000.

These costs could be adjusted to account for changes in the program. For example, by eliminating the PM-10 metal sampling and analysis program, first-year total costs could be reduced by about $73,000 to $88,000.

APPENDIX A

LIST OF TOXIC AIR POLLUTANTS FOR REGIONAL MONITORING PROGRAMS

APPENDIX A

LIST OF TOXIC AIR POLLUTANTS FOR REGIONAL MONITORING PROGRAMS

This appendix includes a list of airborne pollutants for regional air monitoring programs. The list consists of two tables. Table A-1 includes the list of VOCs quantified in the EPA Toxic Air Monitoring Stations (TAMS) program and Table A-2 includes the EPA Urban Air Toxics Monitoring Program Compound List. Table A-3 includes the list of chemicals analyzed under the Houston Regional Monitoring (HRM) program. In addition, you may want to consider other airborne pollutants, particularly those on the list identified in the Community Right to Know Act (otherwise, known as the list in Title III, Section 313 of the Superfund Amendments Reauthorization Act [SARA] of 1986). The lists included in this appendix contain pollutants for which an analytical method is readily available. The SARA 313 list contains pollutants for which new sampling and analytical methods are needed.

TABLE A-1

LIST OF VOLATILE ORGANICS QUANTIFIED IN THE EPA TOXIC AIR MONITORING STATIONS (TAMS) PROGRAM

	Compound Name
1	dichlorodifluoromethane (Freon-12)
2	methyl chloride
3	vinyl chloride
4	trichlorofluoromethane (Freon-11)
5	dichloromethane
6	3-chloropropene
7	1,1,2-trichloro-1,2,2-trifluorethane (Freon-113)
8	1,2-dichloroethane
9	1,1,1-trichloroethane
10	benzene
11	carbon tetrachloride
12	trichloroethene
13	toluene
14	tetrachloroethene
15	chlorobenzene
16	ethylbenzene
17	m-, p-xylene
18	styrene
19	o-xylene
20	4-ethyl toluene
21	1,3,5-trimethylbenzene
22	1,2,4-trimethylbenzene
23	benzyl chloride
24	1,2,4-trichlorobenzene

TABLE A-2

EPA URBAN AIR TOXICS MONITORING PROGRAM COMPOUND LIST

	Compound Name
1	acetylene
2	propylene
3	1,3-butadine
4	vinyl chloride
5	chloromethane
6	chloroethane
7	bromomethane
8	methylene chloride
9	trans-1,2-dichloroethylene
10	1,1-dichloroethane
11	chloroprene
12	bromochloromethane
13	chloroform
14	1,1,1-trichloroethane
15	carbon tetrachloride
16	1,2-dichloroethane
17	benzene/1,2-dichloroethane
18	benzene
19	trichloroethylene
20	1,2-dichloropropane
21	bromodichloromethane
22	trans-1,3-dichloropropylene
23	toluene
24	n-octane
25	n-octane/trans-1,3-dichloropropylene
26	cis-1,3-dichloropropylene
27	1,1,2-trichloroethane
28	tetrachloroethylene
29	dibromochloromethane
30	chlorobenzene
31	ethylbenzene
32	m-, p-xylene
33	styrene/o-xylene
34	bromoform
35	1,1,2,2-tetrachloroethane
36	m-dichlorobenzene
37	p-dichlorobenzene
38	o-dichlorobenzene

TABLE A-3

LIST OF COMPOUNDS INCLUDED IN THE HOUSTON REGIONAL MONITORING (HRM) PROGRAM FOR AIR TOXICS

CAS#		Compound Name	CAS#		Compound Name
74-85-1	1	C-2 VOC	123-72-8	57	butyraldehyde
74-86-2	2	ethylene	96-14-0	58	3-methylpentane
74-84-0	3	acetylene	78-93-3	59	butanone
	4	ethane	763-29-1	60	2-methyl-1-pentene
	5	C-3 VOC	592-41-6	61	1-hexene
115-07-1	6	propylene	760-21-4	62	2-ethyl-1-butene
74-98-6	7	propane	110-54-3	63	n-hexane
74-99-7	8	propyne	7642-09-3	64	cis-3-hexene
74-87-3	9	chloromethane	67-66-3	65	chloroform
75-28-5	10	isobutane	625-27-4	66	2-methyl-2-pentene
75-01-4	11	vinyl chloride	4050-45-7	67	trans-2-hexene
75-07-0	12	acetaldehyde	7688-21-3	68	cis-2-hexene
115-11-7, 106-98-9	13	isobutene, 1-butene	N/A	69	c-3-methyl-2-pentene
			96-37-7	70	methylcyclopentane
106-99-0	14	1,3-butadiene	107-06-2	71	1,2-dichloroethane
106-97-8	15	n-butane	108-08-7	72	2,4-dimethylpentane
74-93-1	16	methyl mercaptan	71-55-6	73	1,1,1-trichloroethane
624-64-6	17	trans-2-butene	590-86-3	74	isovaleraldehyde
74-83-9	18	bromomethane	71-43-2	75	benzene
463-82-1	19	neopentane	27476-50-2	76	methylcyclopentene
107-00-6	20	1-butyne	56-23-5	77	carbon tetrachloride
590-18-1	21	cis-2-butene	110-82-7	78	cyclohexane
75-00-3	22	chloroethane	31394-54-4, 565-59-3	79	isoheptane, 2,3-dimethyl-pentane
67-56-1	23	methanol			
75-71-8	24	dichlorodifluoromethane	110-83-8	80	cyclohexane
563-45-1	25	3-methyl-1-butene	107-87-9	81	2-pentanone
78-78-4	26	Isopentane	78-87-5	82	1,2-dichloropropane
123-38-6	27	propionalydehyde	589-34-4	83	3-methylhexane
67-64-1	28	acetone	71-36-3	84	1-butanol
75-69-4	29	trichlorofloromethane	110-62-3	85	valeraldehyde
109-67-1	30	1-pentene	96-22-0	86	3-pentanone
75-08-1	31	ethyl mercaptan	79-01-6, 75-27-4	87	trichloroethylene + bromodi-chloromethane
503-17-3	32	2-butyne			
64-17-5	33	ethanol	592-76-7	88	1-heptene
563-46-2	34	2-methyl-1-butene	540-84-1	89	2,2,4-trimethylpentane
109-66-0	35	n-pentane	123-91-1	90	1,4-dioxane
78-79-5	36	isoprene	109-79-5	91	Butyl Mercaptan
N/A	37	dimethylsulfide	592-78-9	92	3-heptene
75-05-8	38	acetonitrile	142-82-5	93	n-heptane
75-35-4	39	1,1-dichloroethylene	592-77-8	94	2-heptene
646-04-8	40	trans-2-pentene		95	bichloromethyl ether
60-29-7	41	diethyl ether	107-39-1	96	2,4,4-trimethyl-1-pentene
627-20-3	42	cis-2-pentene	108-87-2	97	methylcyclohexane
513-35-9	43	2-methyl-2-butene	10061-01-5	98	cis-1,3-dichloropropene
75-09-2	44	methylene chloride	107-40-4	99	2,3,4-trimethyl-2-pentene
67-63-0	45	2-propanol	108-10-1	100	methylisobutylketone
75-83-2	46	neohexane	592-13-2	101	2,5-dimethylhexane
78-84-2	47	isobutyraldehyde	110-75-8	102	2-chloroethyl vinyl ether
142-29-0	48	cyclopentene	10061-02-6	103	trans-1,3-dichloropropene
691-37-2	49	4-methyl-1-pentene	79-00-5	104	1,1,2-trichloroethane
287-92-3	50	cyclopentane	565-75-3	105	2,3,4-trimethylpentane
156-60-5	51	trans-1,2-dichoroethylene	554-14-3	106	2-methylthiophene
79-29-8	52	2,3-dimethylbutane	108-88-3	107	toluene
73513-42-5	53	isohexane	616-44-4	108	3-methylthiophene
691-38-3	54	cis-4-methyl-2-pentene	591-49-1	109	1-methylcyclohexene
674-76-0	55	Trans-4-methyl-2-pentene	124-48-1	110	dibromochloromethane
71-23-8	56	1-propanol	N/A	111	3,5,5-trimethylhexene

TABLE A-3 (Cont.)

LIST OF COMPOUNDS INCLUDED IN THE HOUSTON REGIONAL MONITORING (HRM) PROGRAM FOR AIR TOXICS

CAS#		Compound Name	CAS#		Compound Name
589-81-1	112	3-methylheptane	872-05-9	146	1-decene
66-25-1	113	hexanal	106-46-7	147	p-dichlorobenzene
110-01-0	114	tetrahydrothiophene	538-93-2	148	isobutylbenzene
3522-94-9	115	2,2,5-trimethylhexane	124-18-5	149	n-decane
111-66-0	116	1-octene	526-73-8	150	1,2,3-trimethylbenzene
127-18-4	117	tetrachloroethylene	95-50-1	151	o-dichlorobenzene
111-65-9	118	n-octane	99-87-6	152	p-isopropyltoluene
7642-04-8	119	cis-2-octene	496-11-7	153	indan
541-31-1	120	isopentyl mercaptan	95-13-6	154	Indene
108-90-7	121	chlorobenzene	138-86-3	155	limonene
100-41-4	122	ethylbenzene	141-93-5	156	m-diethylbenzene
106-42-3, 108-3-3	123	p-xylene + m-xylene	104-51-8	157	n-butylbenzene
			105-05-5	158	p-diethylbenzene
100-42-5	124	styrene	821-95-4	159	1-undecene
95-47-6	125	o-xylene	1120-21-4	160	n-undecane
79-34-5, 75-25-2	126	1,1,2,2-tetrachloroethane + bromoform	91-20-3	161	naphthalene
			75-34-3	162	1,1-dichloroethane
124-11-8	127	1-nonene	74-82-8	163	methane
2198-23-4	128	4-nonene	100-52-7	164	benzaldehyde
638-02-4	129	2,5-dimethylthiophene	107-13-1	165	acrylonitrile
111-84-2	130	n-nonane	156-59-2	166	cis-1,2-dichloroethylene
98-82-8	131	isopropylbenzene	108-94-1	167	cyclohexanone
80-56-8	132	a-pinene	106-93-4	168	1,2-dibromoethane
95-49-8	133	o-chlorotoluene	110-02-1	169	thiophene
108-41-8	134	m-chlorotoluene	564-02-3	170	2,2,3-trimethylpentane
106-43-4	135	p-chlorotoluene	126-99-8	171	chloroprene
103-65-1	136	n-propylbenzene	67-72-1	172	hexachloro Ethane
620-14-4	137	m-ethyltoluene	74-88-4	173	methyl Iodide
622-96-8	138	p-ethyltoluene	75-56-9	174	propylene Oxide
111-44-4	139	dichloroethyl ether	593-60-2	175	vinyl bromide
108-67-8	140	1,3,5-trimethylbenzene	1634-04-4	176	methy-t-butyl ether
611-14-3	141	o-ethyltoluene	98-87-3	177	benzal chloride*
127-91-3	142	b-pinene	100-44-7	178	benzyl chloride*
98-06-6	143	t-butylbenzene	75-21-8	179	ethylene oxide*
95-63-6	144	1,2,4-trimethylbenzene	87-61-6	180	1,2,3-trichlorobenzene*
541-73-1	145	m-dichlorobenzene	120-82-1	181	1,2,4-trichlorobenzene*

*These compounds may be more difficult to analyze. Validation cannot be assured at this time.

APPENDIX B

HAZARD INDEX METHODOLOGY

APPENDIX B

HAZARD INDEX METHODOLOGY

This appendix outlines methods for ranking and selecting constituents in the regional air monitoring program. This ranking procedure is designed to help the user determine which constituents, from a large list of constituents, to include in the regional air monitoring program. Generally, the reader must select compounds before determining what equipment and analytical methods are used during the regional air monitoring study.

The process detailed in this appendix involves calculating a Constituent Ranking Index (CRI) for each constituent included in Appendix A. The CRI index uses the expected annual average concentration for a compound (e.g. from air dispersion/modeling or monitoring) and compares these expected levels to some criteria that estimates the potential impact on human health. The human health criteria used in the ranking process should be widely available and should reflect an appropriate measure of potential impact. Among the various references used to obtain health values are:

- The EPA's Integrated Risk Information System (IRIS), which is EPA's database for health risk assessment values. This database is accessible via computer.
- National Library of Medicine Network, specific databases such as TOXLINE®, TOXNET®, Hazardous Substance Data Base (HSDB). This network is available through Dialogue® and can be accessed via computer.
- The U.S. EPA Health Effects Assessment Summary Tables, First Quarter FY 89 and updates.

Please note that not all of these databases are peer-reviewed. Therefore, readers should search and review original studies and individual sources.

The health oriented levels shown in the examples that follow are based on the assumption of chronic exposure to an individual contaminant. In the following examples RfD's[1] (EPA reference doses) will be used for non-carcinogens, and a multiple of the inhalation RsD[2] and/or NOEL[3] will be used for compounds that are animal carcinogens. These types of calculations can include all constituents under consideration.

Calculating CRI for Non-Carcinogens Assuming Chronic Exposure

The following examples illustrate calculations of CRIs for *non-carcinogens*. These examples use calculated annual concentrations derived by a dispersion model.

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Example 1:

The RfD value[4] for lead is: 1.5 μ g/m^3. Assume the calculated annual average lead concentration in the community, as determined from dispersion modeling, is 0.2 μ g/m^3. Then the CRI for lead is:

$$\text{CRI (lead)} = \frac{\text{Annual Concentration}}{\text{RfD}} = \frac{0.2}{1.5} = 0.13$$

Example 2:

The RfD value for mercury is 0.5 μ g/m^3. Assume the calculated annual average mercury concentration on the community, as determined from dispersion modeling, is 0.1 μ g/m^3. Then the CRI for mercury is:

$$\text{CRI (mercury)} = \frac{\text{Annual Concentration}}{\text{RfD}} = \frac{0.1}{0.5} = 0.2$$

Calculating the CRI for Carcinogens.

The following are examples for calculating the CRI for *carcinogens*. These examples use calculated annual concentrations derived by a dispersion model.

Example 3:

The reference value (RsD X100) for dichloromethane is 200 μ g/m^3. Assume the calculated annual average dichloromethane concentration in the community, as determined from dispersion modeling, is 4 μg/m3. Then the CRI for dichloromethane is:

$$\text{CRI (dichloromethane)} = \frac{\text{Concentration}}{\text{reference value}} = \frac{4}{200} = .02$$

[1]The RfD (inhalation) is a benchmark dose derived from the NOAEL (No-Observed-Adverse-Effect-Level) by consistent application of order of magnitude uncertainty factors. If an inhalation RfD is not available, it can be calculated as 10^{-6}/unit risk number μg/m^3.

[2]The RsD is the dose corresponding to a 10^{-6} upperbound on risk.

[3]Another measure which has been used is the ED_{10} value, the estimated dose corresponding to a 10% tumor incidence in animals.

Example 4:

The reference value (RsD X100) for trichloroethylene is 60 μ g/m^3. Assume the calculated annual average trichloroethylene concentration in the community, as determined from dispersion modeling, is 10 μ g/m^3. Then the CRI for trichloroethylene is:

CRI (trichloroethylene) =

$$\frac{\text{Concentration}}{\text{reference value}} = \frac{10}{60} = 0.17$$

Example 5

The reference value (NOEL/100) for carbon tetrochloride is 60 μ g/m^3. Assume the calculated annual averge carbon tetrachloride concentration in the community, as determined from dispersion modeling, is 10 μ g/m^3. Then the CRI for carbon tetrachloride is:

CRI (carbon tetrachloride) =

$$\frac{\text{Concentration}}{\text{reference value}} = \frac{10}{60} = 0.17$$

Conclusion

Once the CRI calculations are completed, the sets of CRIs for carcinogens and non-carcinogens are ranked from highest to lowest. The resulting prioritized list should blend carcinogens and non-carcinogens in the ranking. To achieve this blending, it is recommended that for ratios based upon the:

RsD, the RsD should be multiplied by 100 (corresponding to 10^{-4} upperbound estimate of risk).

NOEL, an appropriate fraction of a NOEL must be evaluated to appropriately compare compounds. If NOEL's are consistently used for all compounds, the fraction is immaterial since the relative comparison will be valid. However, if the reader mixes health criteria, a NOEL/100 is recommended to be consistent with the RfD. For direct acting genotoxic carcinogens NOEL/1000 has also been recommended.

Using the examples above for non-carcinogens the CRI for lead is less than the CRI for mercury. Using the examples for carcinogens the CRIs for trichloroethylene and carbon tetrachloride are greater than the CRI for dichloromethane. After this process, the reader can evaluate the project's priorities and select the list of constitutents for the community air toxics monitoring.

[4]Value used is NAAQS.

APPENDIX C

REGIONAL AIR MONITORING METHODS AND EQUIPMENT

NOMENCLATURE USED IN THIS APPENDIX

GC	Gas Chromatograph
FID	Flame Ionization Detector
PID	Photoionization Detector
ECD	Electron Capture Detector
FPD	Flame Photometric Detector
MS	Mass Spectroscopy
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectroscopy
GC-MS-SIM	Gas Chromatography-Mass Spectroscopy-Selected Ion Monitoring
GC-MS-SCAN	Gas Chromatography-Mass Spectroscopy-full SCAN mode
PDFID	Preconcentration and Direct Flame Ionization Detector
HPLC	High Performance Liquid Chromatography
AA	Atomic Absorption
ICP	Inductive Coupled Plasma
FT/IR	Fourier Transform/Infra Red
Hi Vol	High Volume
GFF	Glass Fiber Filter
GFA	Graphite Furnace Atomization
MCEF	Mixed Cellulose Ester Filter (Membrane Filter)
ISE	Ion Selective Electrode
FI	Flame Ionization
DNPH	Dinitrophenylhydrazine
IC	Ion Chromatography

APPENDIX C

REGIONAL AIR MONITORING METHODS AND EQUIPMENT

TABLE C-1
LIST OF AIR TOXIC MONITORING REFERENCES

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2. U.S. EPA. April 1984. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air and Subsequent Updates.* EPA 600/4-84-041. Office of Research and Development. Research Triangle Park, North Carolina 27711.

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13. APHA. 1977. *Methods of Air Sampling and Analysis.* American Public Health Association. Washington, D.C. 20005.

14. ACGIH. 1983. *Air Sampling Instruments for Evaluation of Atmospheric Contaminants.* American Conference of Governmental Industrial Hygienists. Cincinnati, Ohio 45211.

TABLE C-2

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT MONITORING: VOLATILE OPRGANICS

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
CRYOGENIC PRECONCENTRATION/GC/FID/EC--Known volume of air is collected accurately onto a cryogenically cooled trap. Carrier gas transfers the condensed sample to a GC column. Adsorbed compounds are eluted from the GC column and measured by FID or EC detectors.	TO-3	0.1 ppbv (100 ml sample)	90 - 110%	± 15%	• Collects wide variety of volatile organic compounds • Standard procedures are available • Contaminants common to adsorbent materials are avoided • Low blanks	• Moisture levels in air can cause freezing problems • Difficult to use in field • Expensive
CARBON MOLECULAR SIEVE ADSORPTION AND G/MS or GC/FID--Selected volatile organic compounds are captured on carbon molecular sieve adsorbents Compounds are thermally desorbed and analyzed by GC/MS techniques.	TO-2	1 - 200 pptv (20 ml sample)	70 95% (biased low)	± 10 - 40%	• Trace levels of volatile organic compounds are collected and concentrated on sorbent material • Atmospheric moisture not collected.	• Some trace levels of organic species are difficult to recover from the sorbent.
TENAX GC ADSORPTION AND GC/MS OR GC/FID--Ambient air is drawn through organic polymer sorbent where certain compounds are trapped. The cartridge is transferred to the laboratory for analysis. Using GC/MS or GC/FID.	TO-1	0.01 - 1 ppbv (20 ml sample)	80 100%	± 20%	• Good volume of air can be sampled • Water vapor is not collected • Wide variety of compounds collected • Standard procedures available	• Highly volatile compounds and certain polar compounds are not collected. • Breakthrough of compounds could become a major issue for sampling period exceeding 8 hours.
SUMMA PASSIVATED CANISTER AND GC/FID/ECD OR GC/MS--Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.	TO-14	0.1 - 4 ppb	90 - 110%	± 10%	• Best method for broad speciation of unknown trace volatile organics • Simple sampling approach	• Sample components may be adsorbed or decompose through interaction with container walls • Condensation may be a problem at high concentrations (ppm) • Complex equipment preparation required

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100).

TABLE C-3

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT MONITORING: VOLATILE HALOGENATED HYDROCARBONS

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
TENAX GC ADSORPTION AND GC/MS OR GC/ECD--Ambient air is drawn through a cartridge containing Tenax where certain volatile organic compounds are adsorbed. Compounds are transferred by programmed thermal desorption into a GC and detected by MS or ECD.	TO-1	0.01 - 1 ppb	80 - 100%	± 20%	• Moisture is not collected • Large sample volume can be concentrated • Documented standard procedures available with extensive QA/QC data base • Practical for field use • Low detection limits	• Contamination problems possible • Artifact formation problems • Rigorous cleanup required • No possibility of multiple analyses • Low breakthrough volumes for some compounds
CARBON MOLECULAR SIEVE ADSORPTION AND GC/MS OR GC/ECD--Ambient air is drawn through a cartridge containing carbon molecular sieve where highly volatile compounds are adsorbed. Compounds are thermally desorbed to a GC where they are quantitatively measured using MS or EC detectors.	TO-2	1 - 200 pptv (20 ml sample)	70 - 95%	± 10-40%	• Efficient collection of polar compounds • Wide range of application • Highly volatile compounds are adsorbed • Easy to use in field	• Water collected and can deactivate adsorption sites • Thermal desorption of compounds may be difficult
CRYOGENIC TRAPPING AND GC/ECD--Vapor phase organics are condensed in a cryogenic trap. Carrier gas transfers the condensed sample to a GC column. Adsorbed compounds are eluted from the GC column and determined by MS or EC detectors.	TO-3	0.1 ppbv (100 ml sample)	90 - 110%	± 10%	• Large data base • Excellent long-term storage • Wide applicability • Allows multiple analyses • Best method for broad speciation of unknown VOCs • Easy sample collection • Consistent recoveries	• Moisture condensation • Integrated sampling is difficult
SUMMA PASSIVATED CANISTER AND GC/FID/ECD OR GC/MS--Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.	TO-14	0.1 - 4 ppb	90 - 110%	± 10%	• Best method for broad speciation of unknown trace volatile organics • Simple sampling approach	• Sample components may be adsorbed or decompose through interaction with container walls • Condensation may be a problem at high concentrations (ppm) • Complex equipment preparation required

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100).

TABLE C-4

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: VOLATILE OXYGENATES

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
SUMMA PASSIVATED CANISTER AND GC/FID/EC OR GC/PID/EC OR GC/MS--Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatized, separated on a GC column and passed to one or more detectors for identification and quantitation	TO-14 TO-3	0.5 - 20 ppb 0.5 - 20 ppb	90 - 110% 90 - 110%	± 10% ± 20%	• Low cost • High sensitivity • Positive compound ID	• Calibration time consuming • Compound identification is not absolute • Low sensitivity • Expensive
AIR SAMPLE DRAWN THROUGH DINITROPHENYLHYDRAZINE IMPINGER SOLUTION USING A LOW VOLUME PUMP--The solution is analyzed using HPLC with a UV detector.	TO-5	1 - 5 ppbv	80 - 120%	± 10%	• Specific for aldehydes and ketones • Good stability for derivative compounds formed • Low detection limits	• Sensitivity limited by reagent priority • Potential for evaporation of liquid over long term
AIR STREAM DRAWN THROUGH A TENAX CARTRIDGE AND ADSORBED TO IT--Desorption from Tenax is by thermal desorption to GC/MS or GC/FID.	TO-1	1 - 5 ppbv	75 - 125%	± 15 - 20%	• Collect and concentrate large volume sample with trace concentration • Moisture is not a problem • Broad use-reference methods • Low detection limit • Easy to use in field	• Blank contaminants may be a problem • Single analysis per sample • Artifact formations with time
COLLECTION OF WHOLE AIR SAMPLES IN SUMMA PASSIVATED STAINLESS STEEL CANISTERS--VOCs are separated by GC methods and measured by MS or multi-detector techniques.	TO-14	1 ppbv			• Must calibrate separate detectors • Compound identification not positive. Lengthy data interpretation. Does not differentiate targeted compounds from interfering compounds. • GC/multi detector, lower cost than GC-MS • GC/MS - Positive compound identification • More sensitive than MS	• Operator skill level important • Problems may exist with the collection of ethylene oxide and butadiene • Complex equipment preparation required

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100).

TABLE C-5

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: SEMI-VOLATILE PHENOLICS

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
SODIUM HYDROXIDE LIQUID IMPINGER AND HPLC/UV--Ambient air is drawn through 2 midget impingers. Phenols are trapped as phenolates in NaOH solution and analyzed by HPLC.	TO-8	1 ppb	75 - 125%	± 20%	• 4,6-dinitro-2-methylphenol (50/1600) specific to class of compounds • Good stability • Detect non-volatile as well as volatile compounds	• Subject to interferences • Limited sensitivity
ADSORPTION ON TENAX AND GC/FID OR GC/MS--Ambient air is drawn organic polymer sorbent where certain organic compounds are trapped. The cartridge is transferred to the laboratory for analysis. Compounds are desorbed by heating.	TO-1	1 - 200 ppt	70 - 95%	± 10 - 40%	• Good QA/QC data base • Wide range of application • Easy to use in field	• Desorption of some compounds difficult • Blank contamination possible • Artifact formation on adsorbent • High humidity reduces collection efficiency
HIGH VOLUME AND PUF SAMPLER AND GC/ECD--Sorption onto PUF followed by solvent extraction.	TO-4	0.2 - 2 ng/m^3	60 - 100%	± 20%	• Wide range of application • Easy to use - low blanks • Excellent collection and retention efficiencies	• Possibility of contamination • Loss of organics during storage

TABLE C-6

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: SEMI-VOLATILE PESTICIDES/PCBs

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
HIGH VOLUME GLASS FIBER AND PUF CARTRIDGE SAMPLER AND GC/ECD--Compounds solvent extracted and analyzed using GC/ECD.	TO-4	0.2 - 200 ng/m^3	28 to 85 - 100%	± 15%	• Broad range of application • Low blanks • Easy to use • Reusable • High sensitivity	• Can loose volatile compounds in storage • Possibility of contamination
HIGH VOLUME GLASS FIBER FILTER AND XAD-2 CARTRIDGE SAMPLER--Compounds are solvent extracted and analysis completed using GC/MS.	TO-4 (modification)	0.2 - 200 ng/m^3	80 - 120%	± 20%	• Can analyze broad range of compounds (more efficient than PUF) • Easy to clean • Good retantion of compounds	• Possible contamination • Loss of organics during storage
LOW VOLUME PORTABLE SAMPLES WITH PUF CARTRIDGE--Compounds are analyzed with GC/ECD.	TO-11	0.01 - 50 µg/m^3	85 - 100%	± 15%	• Basically the same as for TO-14 above	• Basically the same

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100).

TABLE C-7

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: BENZO(a) PYRENE, [B(a)P] AND OTHER PAHS

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
HIGH VOLUME QUARTZ FILTER AND XAD-2 OR PUF CARTRIDGE SAMPLER WITH GC WITH FLAME IONIZATION (FI) AND MS.	TO-13	<100 pg/m^3	80 - 120%	± 15%	• Effective for broad range of compounds • Easy to preclean and extract • Low blanks	• Possible contamination • Loss of volatile organics during storage
HIGH VOLUME QUARTZ FILTER AND XAD-2 OR PUF CARTRIDGE SAMPLER--Samples are solvent extracted and analyzed using HPLC.	TO-13	<100 pg/m^3	95 - 105%	± 15%	• Effective for broad range of compounds • Easy to clean • Broad data base • Good retention of compounds	• Possible contamination • Loss of organics during storage

TABLE C-8

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: FORMALDEHYDE, ALDEHYDES, AND KETONES

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
SORPTION ON SILICA GEL CARTRIDGE COOLED WITH ACIDIFIED DNPH--Compounds are analyzed by HPLC.	TO-11	1 - 20 ppb	>80%	± 10%	• Low detection limit • Simple collection equipment	• Possible background contamination • Interferences

TABLE C-9

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: VOLATILE INORGANICS

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
HIGH VOLUME GLASS FIBER FILTER AND PUF CARTRIDGE SAMPLER --Particulates are removed from air stream with a GFF or PUF filter, dissolved and analyzed by spectrometric methods including AA/ICP.	TO-4	1 - 5 ng/m^3	± 25%	± 10%	• Wide range of applications • Standard methods • Low detection limits	• Possible interferences
VAPOR PHASE METALS (Sb, As, Pb, Ni, Se, Ag, Hg) IMPINGER--Collection of vapor phase metals on sorbents and in impinger solutions and analyzed by AA/ICP.		1 - 5 ng/m^3			• Standard methods • High sensitivity • QA/QC data base available • Specific method for each metal	• Possible breakthrough • High blanks • Interferences
VAPOR PHASE CN--MCEF and Sodium Hydroxide Liquid Impinger	TO-8, ISE or EPA Method 335.1 or 335.3	1 - 5 ng/m^3			• Standard methods for each metal	• Potential interferences

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100)

TABLE C-10

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR TIME-INTEGRATED AMBIENT AIR MONITORING: AMMONIA, HYDROGEN CHLORIDE AND HYDROGEN SULFIDE

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
AMMONIA IN AMBIENT AIR COLLECTED WITH H_2SO_4 IMPINGER. SAMPLER AND ANALYZED BY IC.	NIOSH/6701	<1ppm	± 20%	± 10%	• Simple collection equipment • Standard analysis method	• Interferences
HC IN AMBIENT AIR IS COLLECTED WITH NaOH IMPINGER SAMPLES AND ANALYZED BY IC.	NIOSH/7903	0.14 - 14ng/m^3	± 20%	± 10%	• Simple collection equipment • Standard analysis method	• Interferences
H_2S IN AMBIENT AIR AND COLLECTED ON MOLECULAR SIEVE THERMALLY ADSORBED AND ANALYZED BY GC/FID.	NIOSH/296 (Proposed)	15 ng/m^3	80 - 100%	± 15%	• Portable sample media • Minimal interference	• Limited holding time from sampling to analysis • Reproducibility of results may vary with each sample collected.

TABLE C-11

SUMMARY OF SAMPLING AND ANALYTICAL METHODS FOR NEAR REAL-TIME AMBIENT AIR MONITORING: DEVELOPING TECHNOLOGIES

Sampling and Analysis Approach	Method Designation	Detection Limit	Accuracy(1)	Precision(2)	Advantages	Disadvantages
MOBILE MASS SPECTROMETER (MS/MS, MS/MS/MS) OR (GC/MS)	None	1 ppb			• Compound identificationin complex mixtures • Direct sampling • Field operation	• Expensive • Skilled operators • Low sensitivity
LONG PATH FT/IR--Remote Optical Volatile Emissions Recorder. Laser source transmitted across contaminated area. Onsite Fourier Transform analyis of reflected laser beam provides organic contaminant analysis by Infrared Spectorometry.	None	ppm-m			• Direct field measurements • Minimum time requirement	• Applicable for source characterization • Does not provide low detection limits • Provides concentration integrated over a path and cannot easily be used in air quality assessment

(1) Accuracy - The Agreement of an analytical measurement with a true or accepted value. Values in this table are expressed as Percent Recovery (%R = Measured Value/True Value x 100).

(2) Precision - The reproducibility of repeated measurements of the same property usually made under prescribed conditions. Values in this table are expressed as Relative Percent Difference (RPD = Range/Mean x 100).

TABLE C-12

SUMMARY OF NEAR-REAL-TIME AMBIENT AIR MONITORING: ORGANIC COMPOUNDS

Sampling and Analysis Approach	Detection Limit	Precision	Mode of Operation	Advantages	Disadvantages
Portable GC analyzer utilizing Argon ionization/electron capture detector (ECD) with optional photoionization detector, preconcentrator and a heated column with temperature adjustable to 140°C. Up to 16 different compounds can be processed at any time. Library is up to 100 compounds. Ongoing calibration is by injecting standard calibration gas.	0.1 to several ppb depending on the number of compounds involved and the mix	About 5-10%, high reproducibility	Real time continuous	• Near-real-time continuous concentrations of air toxic constituents. • Good accuracy and low detection limit for a field technique. • Eliminates inaccuracies associated with the handling of samples obtained by integrator samplers that have to be shipped for laboratory analysis. • Has an option for more than one detector.	• Can analyze only a limited number of air toxic constituents at a time. • Subject to inaccuracies introduced by field conditions and field operators.
Portable GC analyzer utilizing photoionization detector (PID) with a range of 5 different energy lamps to provide selectivity for different chemical groups, isothermal oven control for the multi-capillary column. Up to 25 compounds can be processed at any time. Include four libraries of 25 compounds each. Calibration is by injecting standard calibration gas.	0.1 to several ppb depending on the number of compounds involved and the mix	About 5-10% depending on compound involved, high reproducibility	Real time continuous	• Similar to the ones mentioned above with the exception that it uses only one detector.	• Similar to the ones mentioned above with the addition of: - Isothermal oven control is up to 50°C. This GC cannot operate at higher temperatures. This reduces the range of volatile organics that can be analyzed. Useful mainly for high volatile organics. - Cannot use detectors other than the PID.
Portable GC analyzer can use either a PID or FID. Includes isothermal temperature control of up to 300°C for one model and up to about 200°C for another. Calibrate with either the compounds of interest or with a reference compound. Up to 20 compounds can be processed at any time.	0.1 to several ppb depending on the number of compounds involved and the mix	Not readily available but expected to be in the same range as above	Real time continuous	• Similar to the ones above. • Similar to the ones above with the exception that it uses only a PID detector.	• Similar to ones listed for the portable GC with a ECD with the addition of: - No temperature adjustments - No library for retention times

APPENDIX D

BIBLIOGRAPHY OF AIR MONITORING STANDARD OPERATION PROCEDURES

APPENDIX D

BIBLIOGRAPHY OF AIR MONITORING STANDARD OPERATION PROCEDURES

1. APCA. May 1987. *Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants.* VIP-8. Air Pollution Control Association. Pittsburgh, Pennsylvania 15230.

   These proceedings cover a wide range of topics on recent advances in measurement and monitoring procedures for toxic and related pollutants found in ambient and source atmospheres.

2. APHA. 1977. *Methods of Air Sampling and Analysis.* American Public Health Association (APHA). Cincinnati, Ohio.

   This manual is a comprehensive compilation of standardized methods for sampling and analysis of ambient and workplace air adopted by the APHA Intersociety Committee on Methods of Air Sampling and Analysis.

3. ASTM. 1980. *Sampling and Analysis of Toxic Organics in the Atmosphere.* American Society for Testing and Materials. STP 721. Philadelphia, Pennsylvania.

   This publication resulted from the fourth biennial Boulder, Colorado Conference on environmental monitoring of air quality sponsored by the ASTM. The conference was structured to highlight several major areas of concern to environmental scientists; namely, sampling for toxic organics in ambient, workplace, and source-related atmospheres; analyzing for important classes of pollutants such as polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and polycyclic organic matter (POM); and measuring exposure to toxic organics in the workplace.

4. California Air Resources Board (CARB). February 1985. *Toxic Ambient Air Monitoring Operation Procedures, California Network.* Aerometric Data Division. California Air Resources Board. Sacramento, California 95814.

5. CARB. December 1986. *Testing Guidelines for Active Solid Waste Disposal Sites.* Stationary Source Division. Toxic Pollutants Branch. California Air Resources Board. Sacramento, California 95814.

   These guidelines present standard operating procedures for the sampling and analysis of ambient air collected in Tedlar bags. Analytical procedures are primarily for halogenated volatile organics and benzene.

6. Draeger. May 1985. *Detector Tube Handbook.* Draegerwerk AG Lubeck. Federal Republic of Germany.

   This handbook presents procedures for the use of colorimetric detector tubes for a wide range of organic and inorganic compounds. Data is provided on standard ranges of measurement, precision and accuracy, measurement principles, and cross-sensitivity.

7. NIOSH. February 1984. *NIOSH Manual of Analytical Methods.* NTIS PB85-179018. National Institute of Occupational Safety and Health. Cincinnati, Ohio.

   The NIOSH manuals contain a wealth of information on sampling and analytical procedures for a wide range of toxic organic and inorganic species. Although primarily directed at determination of worker exposure levels, these methods can quite often be applied (with minimal modifications) to the measurement of ambient concentration levels of concern in perimeter and offsite monitoring.

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This document contains a master table for sampling and analytical methods for ambient air monitoring listed by compound name. Key information on species includes recommended sampling and analytical methods, the applicability of each method, performance data, and reference information.

9. South Coast Air Quality Management District (SCAQMD). October 1985. *Guidelines for Implementation of Rule 1150.1.* South Coast Air Quality Management District. Engineering Division. El Monte, California 91731.

   This document contains standard operating procedures for the collection of ambient air samples at landfill perimeters and for instantaneous landfill surface monitoring, as well as analytical procedures for a wide range of toxic volatile organic compounds.

10. U.S. EPA. April 1984. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air and Subsequent Updates.* EPA-600/4-84-041. Office of Research and Development. Research Triangle Park, North Carolina 27711.

    This document contains details for Methods TO-1 through TO-6.

11. U.S. EPA. September 1986. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Supplement and Subsequent Updates.* EPA-600/U-87-006. Office of Research and Development. Research Triangle Park, North Carolina 27711.

    This document contains details for Methods TO-7 through TO-9.

12. U.S. EPA. June 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Supplement and Subsequent Updates.* EPA, Revised June 1988, Office of Research and Development, Research Triangle Park, North Carolina 27711.

    This document contains details for Methods TO-10 through TO-14.

13. U.S. EPA. September 1983. *Characterization of Hazardous Waste Sites - A Methods Manual: Volume II, Available Sampling Methods.* EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

    This volume is a compilation of sampling methods suitable to address most needs that arise during routine waste site and spill investigations. Twelve methods are presented for ambient air, soil gases and vapors, and headspace gases.

14. U.S. EPA. September 1983. *Characterization of Hazardous Waste Sites - A Methods Manual: Volume III, Available Laboratory Analytical Methods.* EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

    This volume provides bench-level guidance for the preparation of hazardous waste, water, soil/sediment, biological tissue, and air samples, and methods that can be used to analyze the resultant digests/extracts of 244 of the substances listed in the RCRA permit regulations.

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27. U.S. EPA. June 1983. *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air.* EPA-600/4-83-027. NTIS PB 83-239020. Office of Research and Development. Research Triangle Park, North Carolina 27711.

28. U.S. EPA. 1977. *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Ambient Air Specific Methods.* EPA-600/4-27-027a. Environmental Monitoring Systems Laboratory. Research Triangle Park, North Carolina 27711.

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The listed appendices to 40 CFR 50 contain EPA Reference Methods for the sampling and analysis of SO_2, TSP, CO, O_3, NO_3, Pb, and PM-10 in ambient air.

APPENDIX E

EXCERPT FROM *TECHNICAL ASSISTANCE DOCUMENT FOR SAMPLING AND ANALYSIS OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR* (U.S. EPA)

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ABSTRACT

This Technical Assistance Document (TAD) was initially published in June 1983 and has been updated to reflect the advances that have been made in sampling and analysis of toxic organic compounds in ambient air. The primary users of this document are expected to be regional, state, and local environmental protection personnel who are faced with the need to determine ambient air quality for regulatory or information-gathering purposes.

The TAD consists of the following seven chapters:

1. Introduction
2. Regulatory Issues Concerning Toxic Organic Monitoring
3. Guidelines for Development of a Monitoring Plan
4. Overview of Sampling Methods
5. Overview of Analytical Methods
6. Methods for Specific Compounds and Compound Classes
7. Quality Assurance

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3.2 DATA QUALITY OBJECTIVES

The first step in any planning process is the identification of objectives. EPA has embraced the process of establishing Data Quality Objectives (DQO's) as a mechanism for ensuring that the quality of environmental data collected under a given program is consistent with the intended use of that data. The DQO process is a three-stage process that places emphasis on defining the regulatory objectives of the environmental monitoring program, the decision that will be made regarding the data collected, and the possible consequences of the decision being incorrect. Experimental design based on DQO's rather than on collection of the "best possible data" is intended to ensure that the information needed to make a decision is obtained, rather than ensuring that each individual measurement obtained is the best possible.

Data quality objectives are statements of the level of uncertainty that a decision maker is willing to accept from results derived from environmental data, when the results are going to be used in a regulatory or programmatic decision such as establishing the need for a new regulation, setting or revising a standard, or determining compliance with an existing standard. Complete data quality objectives must be accompanied by clear statements of:

- The decision to be made.
- Why environmental data are needed.
- How the environmental data will be used.
- Time and resource constraints on data collection.
- Descriptions of the environmental data to be collected.
- Specifications regarding the domain of the decision.
- The calculations, statistical and otherwise, that will be performed on the data in order to arrive at the result.

The DQO process is interactive, consisting of three multi-step stages. The first two stages result in proposed DQO's with accompanying specifications and constraints for designing the data collection system. In the third stage, potential designs for the data collection program are evaluated. The various stages and steps associated with the DQO process are summarized in Table 3.1.

3.2.1 Stage I Activities

This stage is the responsibility of the decision maker: He/she states an initial perception of what decision must be made, what information is needed, why and when it is needed, how it will be used, and what the consequences will be if information of adequate quality is not available. Initial estimates of the time and resources that can reasonably be made available for the data collection activity are presented.

3.2.2 Stage II Activities

This stage is primarily the responsibility of the senior program staff, using guidance and oversight from the decision maker and input from technical staff. The information from Stage I is carefully examined and discussed with the decision maker to ensure that senior program staff understand as many of the nuances of the program as possible. After this interactive process, senior program staff discuss each aspect of the initial problem, exercising their prerogative to reconsider key elements from a technical or policy standpoint. The outcome of their work, once explained to and concurred upon by the decision maker, leads to the generation of specific guidance for designing the data collection program. The products of Stage II include proposed statements of the type and quality of environmental data required to support the decision, along with other technical constraints on the data collection activity, that will place bounds on the search for an acceptable design in Stage III. These outputs are the proposed DQO's.

3.2.3 Stage III Activities

This stage is primarily the responsibility of the technical staff but involves both the senior program staff and the decision maker to assure the outputs from Stages I and II are understood. The objective of Stage III is to develop data collection plans that will meet the criteria and constraints established in Stages I and II. All viable options should be presented to the decision maker. It is the prerogative of the decision maker to select the final design that provides the best balance between time and resources available for data collection and the level of uncertainty expected in the final results.

TABLE 3.1

COMPONENTS OF THE DATA QUALITY OBJECTIVE PROCESS

Stage I	Decision Definition Responsibility: Decision Maker Step 1. Decision Description Step 2. Description of Information Needed for Decision Step 3. Definition of Environmental Data Use Step 4. Definition of Consequences of an Incorrect Decision Attributable to Inadequate Environmental Data Step 5. Description of Available Resources
Stage II	Clarification of the Information Needed for the Decision Responsibility: Senior Program Staff Step 1. Fragmentation of Decision into Decision Elements Step 2. Specification of Required Environmental Data Step 3. Definition of Decision Domain Step 4. Definition of Result to be Derived from Environmental Data Step 5. Definition of Desired Performance Step 6. Evaluation of the Need for New Environmental Data Step 7. Establish the DQO's
Stage III	Design of the Data Collection System Responsibility: Technical Staff Step 1. Development of Viable Data Collection Plans That Meet the Criteria and Constraints Established in Stages I and II.

3.9 QUALITY ASSURANCE PLANNING

The term quality assurance (QA) refers to an overall system design to monitor, document, and control the technical performance of a program. While the need for good QA protocols is widely recognized, the design and implementation of them are frequently treated as secondary parts of the overall monitoring program. If the QA protocols for a monitoring program are to serve a useful purpose, they must (a) be readily implemented within the cost and time constraints of the program and (b) be well understood by the project personnel. Preparation of the QA plan for a monitoring program should be undertaken after the sampling strategy and the sampling and analysis methods have been defined.

An effective QA plan for a TOAP monitoring program must address five basic areas: (a) quality assurance management, (b) sampling quality assurance, (c) analytical quality assurance, (d) data reduction qaulity assurance, and (e) reporting quality assurance. Specific considerations for quality assurance activities in each of these five key areas are summarized in Table 3.2. Each of these topics is addressed thoroughly in Section 7.

TABLE 3.2

QUALITY ASSURANCE (QA) ACTIVITIES SPECIFIED IN PROGRAM PLAN

Quality Assurance (QA) Management

- QA System Design.
- Document Control.
- Data Evaluation and Storage.
- Audit Procedures.
- Corrective Action.
- QA Reports to Program Management.
- Training.

Sampling Quality Assurance

- Site Selection.
- Instrument Calibration and Maintenance.
- Collection of Routine Quality Control Samples.
- Data Recording.
- Sample Labeling, Preservation, Storage, and Transport.
- Chain of Custody Procedures.

Analytical Quality Assurance

- Method Validation Requirements.
- Instrument Calibration and Maintenance.
- Quality Control Sample Analysis.
- Data Recording.

Data Reduction Quality Assurance

- Merging Sampling and Analysis Data Files.
- Storage of Raw and Intermediate Data.
- Data Validation.

Reporting Quality Assurance

- Technical Review of Report.
- Editorial Review of Report.

A series of volumes entitled Quality Assurance Handbook for Air Pollution Measurement Systems (10) serves as a useful, detailed guidance document in the QA area. In particular, Volume I — *Principles* and Volume II — *Ambient Air Specific Methods* may be useful in the field of toxic organic monitoring. Specific guidance for preparation of QA plans is provided in another EPA document (11). QA practices are also discussed in *Methods of Air Sampling and Analysis* (6).

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6. *Methods of Air Sampling and Analysis*, M. Katz, ed., 2nd Edition, American Public Health Association, Washington, D.C., 1977.

10. *Quality Assurance for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1976. V. I - Principles, EPA-600/9-76-005. V. II Ambient Air Specific Methods, EPA-600/4-77-027a.

11. *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plants*, QAMS-005/80, U.S. Environmental Protection Agency, Washington, D.C., December 29, 1980.

SECTION 7

QUALITY ASSURANCE

7.1 QUALITY ASSURANCE EXPECTATIONS

As the discussion of Data Quality objectives in Section 3 indicates, the environmental data used in a decision process must be (1) technically sound and defensible and (2) of sufficient quality to support the decision process. Achievement of DQO's is ultimately accomplished through a Quality Assurance (QA) program. An effective QA program for inclusion in a TOAP monitoring program will consist of planned and systematic activities necessary to establish consistency of the program output with the needs for which the program was established. Program needs can ultimately be understood in terms of acceptable uncertainty associated with the data; a QA program ensures that the limit of uncertainty is within the acceptable boundaries of the data collection program.

The limit of uncertainty will vary with the sampling and analytical procedures. Consequently, there is no universal QA performance standard applicable to all TOAP monitoring programs. It is therefore important to establish QA performance standards consistent with both the intended use of the data and the performance characteristics of the sampling analysis procedures. Failure to reconcile discrepancies that exist between intended data use and QA performance characteristics of the sampling and analytical protocol will undermine the TOAP monitoring program.

7.2 QUALITY ASSURANCE AND QUALITY CONTROL

QA is essentially a management program that addresses delegation of program responsibilities to individuals, documentation, data review, and audits. The objective of QA procedures is to permit an assessment of the reliability of the data. QA activities are typically performed by personnel involved in normal routine operations.

Quality Control (QC) activities complement QA activities. QC activities address sampling procedures, sample integrity, analysis methods, calibration procedures, equipment maintenance procedures, and data production. QC procedures are also performed by individuals involved in the normal routine operations.

7.3 QUALITY ASSURANCE MANAGEMENT

A QA program is essentially a management tool used to ensure that data collected is continually consistent with predetermined quality limits. The major elements of an effective QA program included in a TOAP monitoring program are discussed in the following subsections.

7.3.1 Quality Assurance System Design

Three fundamental elements comprise an effective QA program: First, QA policy and quantitative quality goals or objectives must be defined in a written QA plan. Secondly, organizational structure must accommodate a QA function through job assignments and communication mechanisms. Third, individuals associated with the QA function must have written job descriptions, duties, responsibilities, and authority commensurate with their intended function. Each of these vital QA program components is discussed below:

Before a QA program can be developed, it is necessary to establish a QA policy and establish the objectives of the QA program. Once these fundamental tasks have been accomplished, a QA program can be written to address the strategy for achieving definitive quality objectives relevant to the activities of the organization.

Strategic QA program planning will obviously require an organizational structure conducive to effective QA management. Appropriate considerations for organizational structure include personnel assignments and communication.

Effective QA is accomplished by a separate individual or group within the organization. The individual(s) responsible for QA will have written job descriptions and the corresponding duties, responsibilities, and authority to perform their job functions in a manner that satisfies the QA program requirements.

Although individuals associated with the QA functions are removed from the routine operations they are responsible for assessing, they are by no means totally isolated form those routine operations. Open lines of communication and established communication practices are necessary to ensure interaction between QA personnel, personnel generating data, and personnel assimilating the data. Effective communication is therefore adequately reflected in data output.

7.3.2 Document Control

Because of the volume of written information associated with a TOAP monitoring program, it is necessary to establish procedures for document control, consisting of written procedures for inspection, review, revision, and archival of monitoring program documents. Document control procedures are generally applicable to the following:

- Sampling procedure.
- Calibration procedure.
- Antlytical procedure.
- Data analyses, validation, and reporting procedure.
- Performance and system audit procedure.
- Preventive maintenance procedure.
- The QA program plan.
- QA plans for specific projects.
- Laboratory record notebooks.
- Data sheets.

7.3.3 Data Evaluation

The intent of a QA program is to maintain data continuously within pre-determined quality limits. This objective will not be achieved if information applicable to a QA management activity is not received, reviewed, and/or acted on in a timely manner. An effective QA program will therefore establish what information is required by QA management personnel, how it will be used, when it will be required, when it will be reviewed, and when control actions necessiated by unacceptable data will be implemented.

7.3.4 Standard Reference Materials

The fundamental requirements for producing reliable data are appropriate methodology and properly calibrated instrumentation used according to established procedure. The quality of generated data can be assessed by incorporating reference materials into the sampling and analytical processes.

A reference material is a substance for which critical properties are sufficiently well established for the reference material to be used to calibrate an analyzer or validate a measurement process. Generally speaking, there are three types of reference materials in common use. An internal reference material (ICM) is developed by a laboratory for its own internal use. A certified reference material (CRM) is a reference material issued by an organization recognized by practicing professionals as technically competent to do so. A Standard Reference Material (SRM) is a certified reference material issued by the National Institute of Standards and Technology (NIST). All three types of reference materials are integral components of effective QA programs for TOAP monitoring projects. SRM's are particularly important because they are traceable to national standards and, if used as primary standards, allow meaningful comparisons of data generated by different laboratories or by different sampling and analytical procedures.

SRM's for toxic organic air pollutants at sub PPM and PPB levels were unavailable until recently. Within the past two years, SRM's for several TOAP's at the 5 ppb level have been developed as multi-component mixtures. Information concerning these materials is provided in Appendix E. Whenever possible, these SRM's should be incorporated into the QA program for a TOAP monitoring project.

7.3.5 Quality Audits

Quality auditing tasks are similar to quality control tasks and in some instances may be identical. The significant difference between quality auditing and quality control tasks is that the former are administered by individuals who are not directly involved with the measurement process.

7.3.5.1 Performance Audits

Performance audits are incorporated into a TOAP monitoring program to quantitatively assess the quality of the data being generated by a measurement system. Performance audits include the evaluation of recovery of reference materials through the sampling and analytical equipment and the review of results when test data are entered into a data processing system.

7.3.5.2 System Audits

System audits are incorporated into a TOAP monitoring program to qualitatively assess the quality of data being generated by the measurement system. System audits focus on operational aspects of the measurement process. There aspects include adherence to (a) established sampling and analytical procedures, (b) sample shipment and receipt procedures, (c) equipment maintenance schedules, and (d) quality control and quality audit schedules.

7.3.6 Quality Assurance Reports

A variety of QA reports should be prepared periodically by the QA personnel and submitted to the TOAP monitoring program manager. The frequency and type of report required will be specified by the QA project plan.

Data Quality Assessment Reports address the precision and accuracy of program data. *Performance and System Audit Reports* summarize the results of audits performed during the course of the TOAP monitoring project. *Data Validation Reports* summarize questionable data collected during the monitoring program, the results of follow-up investigations concerning corrective action recommended, and effectiveness of the data validation procedures. *Quality Cost Reports* summarize the costs associated with each element (prevention, appraisal, and failure) of a Quality Cost System for a TOAP monitoring program. *Instrument and/or Equipment Downtime Reports* summarize information concerning instrument and/or equipment failures, failure courses, repair time, and total downtime. *Control Charts* are graphical representations of QA data. Finally, *Interlaboratory Comparison Summary Reports* are published by EPA and are applicable only to specific analytes and methodologies.

7.3.7 Corrective Action

In many cases data review or audit procedures will result in the need for corrective action. This may involve reporting certain aspects of the work or simply providing more detailed documentation for work already performed. In either case QA management will be responsible for documenting the need for, type of, and implementation of corrective action.

7.3.8 Training

An important component of a QA program will involve personnel training. Trained personnel are necessary to ensure that the data they produce are complete and of high quality. Training can be accomplished on the job or by trainees attending courses relevant to the employees' job functions.

The effectiveness of training must be documented to establish and maintain the integrity of the training program. Training effectiveness can be evaluated by written tests, proficiency evaluations, and/or interviews.

7.4 SAMPLING QUALITY ASSURANCE

The purpose of sampling is to collect unbiased samples that are representative of the system being monitored. The sampling program should be planned and documented in all details. QA for sampling includes site selection, number of samples to be collected, frequency of sample collection, sampling times, instrument calibration and maintenance, Quality Control sample collection, data recording, sample labeling, sample preservation, sample storage, sample transport, and chain-of-custody procedures.

7.4.1 Site Selection

Site selection planning is discussed thoroughly in Section 3.3. The QA plan for a TOAP monitoring program should specify factors which could result in modification of the siting plan during the monitoring effort, procedures for approving such modification, and provisions for documenting sampling site modifications.

7.4.2 Instrument Calibration and Maintenance

Calibration of sampling equipment is as vital as calibration of analytical equipment if meaningful data concerning ambient concentrations of TOAP's are to be obtained. A QA plan for a TOAP monitoring program will therefore address calibration of sampling equipment. Typically the QA plan will include:

- Written calibration procedures.
- Calibration frequencies.
- Acceptable calibration quality.
- A statement of the appropriate environment in or conditions for which the sampling equipment can be used.
- Provisions for proper record keeping of calibration data.

The QA plan will also address appropriate maintenance activities and frequencies for sampling equipment, to ensure that it operates as planned. Additionally, the QA plan will address procedures to document performance of maintenance activities on schedule.

7.4.3 Routine Quality Control Sample Collection

A QA plan for a TOAP monitoring project will include a provision for the collectin of a variety of quality control samples. Qualty control samples to check overall system performance may include replicate or split samples, spiked samples, standard reference materials, blanks, and backup snipes (e.g., series impingers or resin cartridges). Split or replicate samples are useful checks on sampling and analysis precision and should be included with each group of samples. Field blanks, in which the sampling activity is duplicated exactly except that no air is sampled, should also be routinely collected. Backup samples should be collected whenever the recovery performance of a particular sampling medium has not been documented or is subject to wide variations depending on ambient conditions. Spiked samples should be included whenever an accurate spiking prcedure is available, provided that the spiked material reasonably simulates the physical and chemical state of the native material.

7.4.4 Sample Labeling, Preservation, Storage, and Transport

The data obtained from a TOAP monitoring program will be meaningless if samples are improperly labeled or if preservation, storage, or transport procedures are inappropriate for the required analyses. Sample labeling, preservation, storage, and transport procedures will therefore be specified in the QA plan, and these procedures should be carefully explained to field personnel, prior to sampling, to ensure proper implementation. Sample labels, prepared in advance, should include sufficient information to associate a given sample with a particular data sheet, as well as with the overall program record notebook. In general, each sample should be given a unique identification number with a prefix describing the type of sample.

7.4.5 Chain-of-Custody Procedure

Chain-of-custody procedures are used to document the movement of a sample from collection until analysis, to ensure sample integrity. Formal chain-of-custody requirements place a substantial burden on both field and laboratory personnel. Chain-of-custody procedures must be documented in the QA plan for a TOAP monitoring project and reviewed with the personnel who will use them, to ensure that the data is fundamentally legally defensible.

7.5 ANALYTICAL QUALITY ASSURANCE

The QA plan for the analytical component of a TOAP monitoring program will address method validation requirements, instrument maintenance and calibration, quality control sample analysis, and data recording. Each of these aspects is discussed in the subsections that follow.

7.5.1 Method Validation

Many TOAP monitoring program will require the development of new or modification of exiting sampling and analytical protocols. It will be necessary to establish the performance characteristics of these procedures, prior to their use in TOAP monitoring programs. Performance characteristics will include determination of precision, accuracy, detection limit, and specificity through the analysis of laboratory standards and, whenever possible, representative samples. The validation requirements should be appropriate. The incorporation of SRM's in the method validation process will prove cost effective and minimize the time required to bring a new method on line. It is important to validate the method in a manner that approximates as closely as possible the conditions that will exist when actual samples are collected.

Performance critria for existing, well documented methodologies must also be validated when a procedure is used for the first time by the test team. Validation of this type will require the development of a data base sufficient to establish critical statistical parameters such as the coefficient of variation. Again, SRM's are a key component of the method validation process.

Finally, method validation procedures, such as the recovery of spiked samples, should be integrated into the daily sampling and analysis program. SRM's, IRM's, or CRS's are appropriate for this form of method validation.

7.5.2 Instrument Calibration and Maintenance

Proper calibration of analytical instrumentation is fundamental to the success of a TOAP monitoring program. The QA plan for a TOAP monitoring program will therefore include a calibration plan for the various analytical systems used on the project. The calibration plan will include:

1. A statement of the maximum allowable time between multipoint calibrations and calibration checks.

2. A statement of the minimum quality of calibration standards (e.g., standards should have four to ten times the accuracy of the instruments that they are being used to calibrate). A list of calibration standards should be provided.

3. Provisions for standard traceability (e.g., standards should be traced to NBS-SRM's or commerical Certified Reference Materials [CRM's] if available).

4. Provisions for written procedures to help ensure that calibrations are always performed in the same manner. The procedures should include the intended range of validity.

5. Statement of proper environmental conditions, to ensure that the equipment is not significantly affected by its surroundings.

6. Provisions for proper record keeping and record forms to ensue that adequate documentation of calibrations is available for use in internal data validation and in case the data are used in enforcement actions.

7. Documentation of qualifications and training of personnel performing calibration.

The QA plan will also address appropriate maintenance activities and frequencies for analytical equipment. Additionally, the QA plan will include procedures to document performance of maintenance activities on schedule.

7.5.3 Quality Control Sample Analysis

A QA plan for a TOAP monitoring project will include provisions for the analysis of a variety of quality control samples. Quality control samples for evaluating analytical performance should include blanks, spiked process lanks, spiked samples, standard reference materials, and replicate (or split) samples. Standard reference materials and replicate or split samples should generally be included as part of field QA and need not be additionally included at the analysis stage. However, additional blanks, spiked process blanks, and spiked samples should be included, since this practice allows matrix effects to be distinguished from analytical losses.

7.6 DATA MANAGEMENT

The QA plan for a TOAP monitoring program will include procedures designed to ensure that required sampling and analytical data are captured and maintained securely and efficiently. Data recording procedures that should be specified in the sampling QA plan include (a) periodic reading of the temperature, flow, volumes, and other parameters; (b) documentation meteorological conditions at appropriate time points; (c) documentation of instrument operating variables; (d) documentation of any upset conditions such as sudden leakage or pressure surges; and (e) documentation of calibration or maintenance activities. A logbook for the overall sampling program, in which sampling descriptions, meteorological data, and upset conditions are documented, should be maintained. A data sheet should also be prepared for each set of samples or analytical procedure for which relevant raw data should be recorded. Certain measurements, such as filter numbers and weights or impinger volumes, which are required for analytical purposes can be recorded on a separate sheet with provisions for recording subsequent analytical data on the same sheet. Separate maintenance and calibration logbooks should be maintained for each instrument. In most cases, specific sampling data forms for a given program must be prepared because of differences in the sampling design between programs.

The QA program for a TOAP monitoring project will address various steps in the data reduction process including:

- Merging sampling and analytical data.
- Storage of raw and intermediate data.
- Data validation.

Since sampling and analytical data processing occurs independently in most cases, the QA plan will address the manner in which data from the two activities are to be treated and validated during the reduction process. Because TOAP monitorin data can be collected over an extended period of time and may involve several parties, it is important that the QA plan address procedures for transferring and storing raw and intermediate data. Finally, the data reduction component of the QA program will set up data validation procedures so that appropriate data validation reports can be prepared.

7.7 REPORTING QUALITY ASSURANCE

The report represents the final output of a TOAP monitoring program. The QA plan will therefore incorporate appropriate review procedures to ensure that the report properly summarizes the results of the study.

The report must be reviewed by individuals capable of recognizing technical ddeficiencies and QA inconsistencies. The report should also be reviewed by project personnel who were involved in data generation. Finally, the report should be reviewed for editorial content, to minimize ambiguities.

APPENDIX E

CALIBRATION GAS STANDARDS

Cylinder gas standards of selected hazardous organic compounds at the ppb level are available through the USEPA for use in auditing the performance ambient air and stationary source measurement systems. Calibration standard ranges are 5 ppb and up. Information can be obtained by contacting:

Robert L. Lampe
USEPA
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, NC 27711
Phone:
Commercial - 919/541-4531
FTS - 629-4531

Group I Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene

Group II Compounds

Trichloroethylene
1,2 - dichloroethane
1,2 - dibromoethane
Acetonitrile
Trichlorofluoromethane (Freon-11)
Dichlorodifluoromethane (Freon-12)
Bromomethane
Methyl ethyl ketone
1,1,1-trichloroethane

Group III Compounds

Vinylidene chloride
1,1,2 trichloro-1,2,2-trifluoro-ethene (Freon-113)
1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
Acetone
1-4 Dioxane
Toluene
Chlorobenzene

Group IV Compounds

Acrylonitrile
1,3-Butadiene
Ethylene oxide
Methylene Chloride
Propylene oxide
ortho-xylene

Group V Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene
Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
Methylene chloride
Trichlorofluoromethane (Freon-11)
Bromomethane
Toluene
Chlorobenzene
1,3-Butadiene
ortho-xylene
Ethyl benzene
1,2-dichloropropane

APPENDIX F

EXAMPLES OF STANDARD OPERATING PROCEDURES (SOPs)

SOPs FOR OPERATING VOCs CANISTER SAMPLER
U.S. EPA COMPENDIUM METHOD T014 (1988)

SOPs FOR METEOROLOGICAL STATION OPERATIONS AND CALIBRATION

COMPENDIUM METHOD TO-14

THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR USING SUMMA ® PASSIVATED CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

QUALITY ASSURANCE DIVISION
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

MAY, 1988

METHOD T014

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR USING SUMMA® PASSIVATED CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

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METHOD T014

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR USING SUMMA® PASSIVATED CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

1.0 Scope

1.1 This document describes a procedure for sampling and analysis of volatile organic compounds (VOCs) in ambient air. The method is based on collection of whole air samples in SUMMA® passivated stainless steel canisters. The VOCs are subsequently separated by gas chromatography and measured by mass-selective detector or multidetector techniques. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

1.2 This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters (1,2). However, minimal documentation is currently available demonstrating stability of VOCs in subatmospheric pressure canisters.

1.3 The organic compounds that have been successfully collected in pressurized canisters by this method are listed in Table 1. These compounds have been successfully measured at the parts per billion by volume (ppbv) level.

2.0 Applicable Documents

2.1 ASTM Standards

D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis
E260 - Recommended Practice for General Gas Chromatography Procedures
E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (3) Laboratory and Ambient Air Studies (4-17)

3.0 Summary of Method

3.1 Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated SUMMA® passivated canister.

3.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis.

3.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

3.4 The analytical strategy for Method T014 involves using a high-resolution gas chromatograph (GC) coupled to one or more appropriate GC detectors. Historically, detectors for a GC have been divided into two groups: non-specific detectors and specific detectors. The non-specific detectors include, but are not limited to, the nitrogen-phosphorus detector (NPD), the flame ionization detector (FID), the electron capture detector (ECD) and the photo-ionization detector (PID). The specific detectors include the mass spectrometer (MS) operating in either the selected ion monitoring (SIM) mode or the SCAN mode, or the ion trap detector. The use of these detectors or a combination of these detectors as part of an analytical scheme is determined by the required specificity and sensitivity of the application. While the nonspecific detectors are less expensive per analysis and in some cases more sensitive than the specific detector, they vary in specificity and sensitivity for a specific class of compounds. For instance, if multiple halogenated compounds are targeted, an ECD is usually chosen; if only compounds containing nitrogen or phosphorus are of interest, a NPD can be used; or, if a variety of hydrocarbon compounds are sought, the broad response of the FID or PID is appropriate. In each of these cases, however, the specific identification of the compound within the class

is determined only by its retention time, which can be subject to shifts or to interference from other nontargeted compounds. When misidentification occurs, the error is generally a result of a cluttered chromatogram, making peak assignment difficult. In particular, the more volatile organics (chloroethanes, ethyltoluenes, dichlorobenzenes, and various freons) exhibit less well defined chromatographic peaks, leading to misidentification using non-specific detectors. Quantitative comparisons indicate that the FID is more subject to error than the ECD because the ECD is a much more selective detector for a smaller class of compounds which exhibits a stronger response. Identification errors, however, can be reduced by: (a) employing simultaneous detection by different detectors or (b) correlating retention times from different GC columns for confirmation. In either case, interferences on the non-specific detectors can still cause error in identifying a complex sample. The non-specific detector system (GC-NPD-FID-ECD-PID), however, has been used for approximate quantitation of relatively clean samples. The nonspecific detector system can provide a "snapshot" of the constituents in the sample, allowing determination of:

- Extent of misidentification due to overlapping peaks,
- Position of the VOCs within or not within the concentration range of anticipated further analysis by specific detectors (GC-MS-SCAN-SIM) (if not, the sample is further diluted), and
- Existence of unexpected peaks which need further identification by specific detectors.

On the other hand, the use of specific detectors (MS coupled to a GC) allows positive compound identification, thus lending itself to more specificity than the multidetector GC. Operating in the SIM mode, the MS can readily approach the same sensitivity as the multidetector system, but its flexibility is limited. For SIM operation, the MS is programmed to acquire data for a limited number of targeted compounds while disregarding other acquired information. In the SCAN mode, however, the MS becomes a universal detector, often detecting compounds which are not detected by the multidetector approach. The GC-MS-SCAN will provide positive identification, while the GC-MS-SIM procedure provides quantitation of a restricted "target compound" list of VOCs.

The analyst often must decide whether to use specific or non-specific detectors by considering such factors as project objectives, desired detection limits, equipment availability, cost and personnel capability in developing an analytical strategy. A list of some of the advantages and disadvantages associated with non-specific and specific detectors may assist the analyst in the decision-making process.

Non-Specific Multidetector Analytical System

Advantages	Disadvantages
• Somewhat lower equipment cost than GC-MS	• Multiple detectors to calibrate
• Less sample volume required for analysis	• Compound identification not positive
• More sensitive - ECD may be 1000 times more sensitive than GC-MS	• Lengthy data interpretation (one hour each for analysis and data reduction)
	• Interference(s) from co-eluting compound(s)
	• Cannot identify unknown compounds - outside range of calibration - without standards
	• Does not differentiate targeted compounds from interfering compounds

Specific Detector Analytical System

GC-MS-SIM

Advantages	Disadvantages
• positive compound identification	• can't identify non-specified compounds (ions)
• greater sensitivity than GC-MS-SCAN	• somewhat greater equipment cost than multidetector GC
• less operator interpretation than for multidetector GC	• greater sample volume required than for multidetector GC
• more specific than the multidetector GC	• can resolve co-eluting peaks
	• universality of detector sacrificed to achieve enhancement in sensitivity

GC-MS-SCAN

• positive compound identification	• lower sensitivity than GC-MS-SIM
• can identify all compounds	• greater sample volume required than for multidetector GC
• less operator interpretation	• somewhat greater equipment cost than multidetector GC
• can resolve co-eluting peaks	

The analytical finish for the measurement chosen by the analyst should provide a definitive identification and a precise quantitation of volatile organics. In a large part, the actual approach to these two objectives is subject to equipment availability. Figure 1 indicates some of the favorite options that are used as an analytical finish. The GC-MS-SCAN option uses a capillary column GC coupled to a MS operated in a scanning mode and supported by spectral library search routines. This option offers the nearest approximation to unambiguous identification and covers a wide range of compounds as defined by the completeness of the spectral library. GC-MS-SIM mode is limited to a set of target compounds which are user defined and is more sensitive than GC-MS-SCAN by virtue of the longer dwell times at the restricted number of m/z values. Both these techniques, but especially the GC-MS-SIM option, can use a supplemental general non-specific detector to verify/identify the Presence of VOCs. Finally, the option labelled GC-multidetector system uses a combination of retention time and multiple general detector verification to identify compounds. However, interference due to nearly identical retention times can affect system quantitation when using this option.

Due to the low concentrations of VOCs encountered in urban air (typically less than 4 ppbv and the majority below 1 ppbv) along with their complicated chromatograms, Method TO-14 strongly recommends the specific detectors (GC-MS-SCAN-SIM) for positive identification and for primary quantitation to ensure that high-quality ambient data is acquired.

For the experienced analyst whose analytical system is limited to the non-specific detectors, Section 10.3 does provide guidelines and example chromatograms showing typical retention times and calibration response factors, and utilizing the non-specific detectors (GC-FID-ECD-PID) analytical system as the primary quantitative technique.

4.0 Significance

4.1 VOCs enter the atmosphere from a variety of sources, including petroleum refineries, synthetic organic chemical plants, natural gas processing plants, and automobile exhaust. Many of these VOCs are acutely toxic; therefore, their determination in ambient air is necessary to assess human health impacts.

4.2 Conventional methods for VOC determination use solid sorbent sampling techniques. The most widely used solid sorbent is Tenax®. An air sample is drawn through a Tenax® -filled cartridge where certain VOCs are trapped on the polymer. The sample cartridge is transferred to a laboratory and analyzed by GC-MS.

4.3 VOCs can also be successfully collected in stainless steel canisters. Collection of ambient air samples in canisters provides (1) convenient integration of ambient samples over a specific time period, (e.g., 24 hours); (2) remote sampling and central analysis; (3) ease of storing and shipping samples; (4) unattended sample collection; (5) analysis of samples from multiple sites with one analytical system; and (6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems. However, care must be exercised in selecting, cleaning, and handling sample canisters and sampling apparatus to avoid losses or contamination of the samples. Contamination is a critical issue with canister-based sampling because the canister is the last element in the sampling train.

4.4 Interior surfaces of the canisters are treated by the SUMMA® passivation process, in which a pure chrome-nickel oxide is formed on the surface. This type of vessel has been used in the past for sample collection and has demonstrated sample storage stability of many specific organic compounds.

4.5 This method can be applied to sampling and analysis of not only VOCs, but also some selected semivolatile organic compounds (SVOCs). The term "semivolatile organic compounds" is used to broadly describe organic compounds that are too volatile to be collected by filtration air sampling but not volatile enough for thermal desorption from solid sorbents. SVOCs can generally be classified as those with saturation vapor pressures at 25°C between 10^{-1} and 10^{-7} mm Hg. VOCs are generally classified as those organics having saturated vapor pressures at 25°C greater than 10^{-1} mm Hg.

5.0 Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D13S6, E260, and E355. All abbreviations and symbols within this method are defined at point of use.

5.1 Absolute canister Pressure = Pg + Pa, where Pg = gauge pressure in the canister (kPa, psi) and Pa = barometric Pressure (see 5.2).

5.2 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg or Psia.

5.3 Cryogen - A refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid oxygen (bp -183.0°C) or liquid argon (bp -185.7°C).

5.4 Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

5.5 Gauge pressure - Pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

5.6 MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves as a qualitative identification and characterization of the sample.

5.7 MS-SIM - The GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using SIM coupled to retention time discriminators. The GC-SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

5.8 Megabore® column - Chromatographic column having an internal diameter (I.D.) greater than 0.50 mm. The Megabore® column is a trademark of the J&W Scientific Co. For purposes of this method, Megabore® refers to chromatographic columns with 0.53 mm I.D.

5.9 Pressurized sampling - Collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

5.10 Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

5.11 Quantitative accuracy - The ability of an analytical system to correctly measure the concentration of an identified compound.

5.12 Static calibration - Calibration of an analytical system using standards in a form different than the samples to be analyzed. An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

5.13 Subatmospheric sampling - Collection of an air sample in an evacuated canister at a (final) canister pressure below atmospheric pressure, without the assistance of a sampling pump. The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection.

6.0 Interferences and Limitations

6.1 Interferences can occur in sample analysis if moisture accumulates in the dryer (see Section 10.1.1.2). An automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air eliminates any moisture buildup. This procedure does not degrade sample integrity.

6.2 Contamination way occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and certifying the field sampling system are described in Sections 12.1 and 12.2, respectively.

6.3 Because the GC-MS analytical system employs a Nafion® permeable membrane dryer to remove water vapor selectively from the sample stream, polar organic compounds may permeate concurrent with the moisture molecule. Consequently, the analyst should quantitate his or her system with the specific organic constituents under examination.

7.0 Apparatus

7.1 Sample Collection
[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxics Air Monitoring Stations (TAMS), Urban Air Toxic Pollutant Program (UATP), and the non-methane organic compound (NMOC) sampling and analysis Program.]

7.1.1 Subatmospheric Pressure (See Figure 2 Without Metal Bellows Type Pump)

7.1.1.1 Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample canister - leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and SUMMA® passivated interior surfaces (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843, or Anderson Samplers, Inc., 4215-C Wendell Dr., Atlanta, GA, 30336, or equivalent).

7.1.1.3 Stainless steel vacuum/pressure gauge - capable of measuring vacuum (-100 to 0 kPa or 0 to 30 in Hg) and pressure (0-206 kPa or 0-30 psig) in the sampling system (Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.1.1.4 Electronic mass flow controller - capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20-40°C) and humidity (Tylan Corp.. 19220 S. Normandie Ave., Torrance, CA 90502, Model FC-260, or equivalent).

7.1.1.5 Particulate matter filter - 2-um sintered stainless steel in-line filter (Nupro Co., 4800 E. 345th St., Willoughby, OH 44094, Model SS-2F-K4-2, or equivalent).

7.1.1.6 Electronic timer - for unattended sample collection (Paragon Elect. Co., 606 Parkway Blvd., P.O. Box 28, Twin Rivers, WI 54201, Model 7008-00, or equivalent).

7.1.1.7 Solenoid valve - electrically-operated, bi-stable solenoid valve (Skinner Magnelatch Valve, New Britain, CT. Model V5RAM49710, or equivalent) with Viton® seat and o-rings.

7.1.1.8 Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #8125, or equivalent). All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel.

7.1.1.9 Thermostatically controlled heater - to maintain temperature inside insulated sampler enclosure above ambient temperature (Watlow Co., Pfafftown, NC, Part 04010080. or equivalent).

7.1.1.10 Heater thermostat - automatically regulates heater temperature (Elmwood Sensors, Inc., 500 Narragansett Park Dr., Pawtucket RI 02861, Model 3455-RC-0100-0222, or equivalent).

7.1.1.11 Fan - for cooling sampling system (EG&G Rotron, Woodstock, NY, Model SUZAI, or equivalent).

7.1.1.12 Fan thermostat - automatically regulates fan operation (Elmwood Sensors, Inc., Pawtucket, RI, Model 3455-RC-0100-0244, or equivalent).

7.1.1.13 Maximum-minimum thermometer - records highest and lowest temperatures during sampling period (Thomas Scientific, Brooklyn Thermometer Co., Inc., P/N 9327H30, or equivalent).

7.1.1.14 Nupro stainless steel shut-off valve - leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary vacuum pump - continuously draws ambient air to be sampled through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted. [Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed time meter - measures duration of sampling (Conrac, Cramer Div., Old Saybrook, CT, Type 6364, P/N 10082, or equivalent).

7.1.1.17 Optional fixed orifice, capillary, or adjustable micrometering valve - may be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (Figure 2 With Metal Bellows Type Pump and Figure 3)

7.1.2.1 Sample pump - stainless steel, metal bellows type (Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067, Model MB-151, or equivalent), capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds. [Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Center (18,19) and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensating flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet. Interferences using this configuration have been minimal.]

7.1.2.2 Other supporting materials - all other components of the pressurized sampling system (Figure 2 with metal bellows type pump and Figure 3) are similar to components discussed in Sections 7.1.1.1 through 7.1.1.16.

7.2 Sample Analysis

7.2.1 GC-MS-SCAN Analytical System (See Figure 4)

7.2.1.1 The GC-MS-SCAN analytical system must be capable of acquiring and processing data in the MS-SCAN mode.

7.2.1.2 Gas chromatograph - capable of sub-ambient temperature programming for the oven, with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. Flame ionization detector optional. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent.)

7.2.1.3 Chromatographic detector - mass-selective detector (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, Model HP-5970 MS, or equivalent), equipped with computer and appropriate software (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, HP-216 Computer, Quicksilver MS software, Pascal 3.0, mass storage 9133 HP Winchester with 3.5 inch floppy disk, or equivalent). The GC-MS is set in the SCAN mode, where the MS screens the sample for identification and quantitation of VOC species.

7.2.1.4 Cryogenic trap with temperature control assembly - refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC, 27704, Model 320-01, or equivalent).

7.2.1.5 Electronic mass flow controllers (3) - maintain constant flow (for carrier gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.1.6 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (Thomas Industries, Inc., Sheboygan, WI, Model 107BA20, or equivalent).

7.2.1.7 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings -refer to Section 7.1.1.8 for description.

7.2.1.8 Chromatographic column - to provide compound separation such as shown in Table 5 (Hewlett Packard, Rt. 41, Avondale, PA 19311, GV-I capillary column, 0.32 mm x 50 m with 0.88 um crosslinked methyl silicone coating, or equivalent).

7.2.1.9 Stainless steel vacuum/pressure gauge (optional) - capable of measuring vacuum (-101.3 to 0 kPa) and pressure (0-206 kPa) in the sampling system (Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.2.1.10 Stainless steel cylinder pressure regulators - standard, two-stage cylinder regulators with pressure gauges for helium, zero air and hydrogen gas cylinders.

7.2.1.11 Gas purifiers (3) - used to remove organic impurities and moisture from gas streams (Hewlett Packard, Rt. 41, Avondale, PA, 19311, P/N 19362 - 60500, or equivalent).

7.2.1.12 Low dead-volume tee (optional) - used to split the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.2.1.13 Nafion® dryer - consisting of Nafion tubing coaxially mounted within larger tubing (Perma Pure Products, 8 Executive Drive, Toms River, NJ, 08753, Model MD-125-48, or equivalent). Refer to Section 10.1.1.2 for description.

7.2.1.14 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.1.15 Chart recorder (optional) - compatible with the detector output signals to record optional FID detector response to the sample.

7.2.1.16 Electronic integrator (optional) - compatible with the detector output signal of the FID and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.2 GC-MS-SIM Analytical System (See Figure 4)

7.2.2.1 The GC-MS-SIM analytical system must be capable of acquiring and processing data in the MS-SIM mode.

7.2.2.2 All components of the GC-MS-SIM system are identical to Sections 7.2.1.2 through 7.2.1.16.

7.2.3 GC-Multidetector Analytical System (See Figure 5 and Figure 6)

7.2.3.1 Gas chromatograph with flame ionization and electron capture detectors (photoionization detector optional) - capable of sub-ambient temperature programming for the oven and simultaneous operation of all detectors, and with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent).

7.2.3.2 Chart recorders - compatible with the detector output signals to record detector response to the sample.

7.2.3.3 Electronic integrator - compatible with the detector output signals and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.3.4 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.3.5 Cryogenic trap with temperature control assembly - refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC 27704, Model 320-01, or equivalent).

7.2.3.6 Electronic mass flow controllers (3) - maintain constant flow (for carrier gas, nitrogen make-up gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.3.7 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (see 7.2.1.6 for source and description).

7.2.3.8 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings -refer to Section 7.1.1.8 for description.

7.2.3.9 Chromatographic column - to provide compound separation such as shown in Table 7. (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-1 capillary column, 0.32 mm x 50 m with 0.88 um crosslinked methyl silicone coating, or equivalent). [Note: Other columns (e.g., DB-624) can be used as long as the system meets user needs. The wider Megabore® column (i.e., 0.53 mm I.D.) is less susceptible to plugging as a result of trapped water, thus eliminating the need for a Nafion® dryer in the analytical system. The Megabore® column has sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (i.e., 0.32 mm I.D.).

7.2.3.10 Vacuum/pressure gauges (3) - refer to Section 7.2.1.9 for description.

7.2.3.11 Cylinder pressure stainless steel regulators - standard, two-stage cylinder regulators with pressure gauges for helium, zero air, nitrogen, and hydrogen gas cylinders.

7.2.3.12 Gas purifiers (4) - used to remove organic impurities and moisture from gas streams (Hewlett-Packard, Rt. 41, Avondale, PA, 19311, P/N 19352 - 60500, or equivalent).

7.2.3.13 Low dead-volume tee - used to split (50/50) the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.3 Canister Cleaning System (See Figure 7)

7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <0.05 mm Hg.

7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.

7.3.3 Shut-off valve(s) - seven (7) on-off toggle valves.

7.3.4 Stainless steel vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 0.05 mm Hg or less.

7.3.5 Cryogenic trap (2 required) - stainless steel U-shaped open tubular trap cooled with liquid oxygen or argon to prevent contamination from back diffusion of oil from vacuum pump and to provide clean, zero air to sample canister(s).

7.3.6 Stainless steel pressure gauges (2) - 0-345 kPa (0-50 psig) to monitor zero air pressure.

7.3.7 Stainless steel flow control valve - to regulate flow of zero air into canister(s).

7.3.8 Humidifier - pressurizable water bubbler containing high performance liquid chromatography (HPLC) grade deionized water or other system capable of providing moisture to the zero air supply.

7.3 9 Isothermal oven (optional) for heating canisters (Fisher Scientific, Pittsburgh, PA, Model 349, or equivalent).

7.4 Calibration System and Manifold (See Figure 8)

7.4.1 Calibration manifold - glass manifold, (1.25 cm I.D. x 66 cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing.

7.4.2 Humidifier - 500-mL impinger flask containing HPLC grade deionized water.

7.4.3 Electronic mass flow controllers - one 0 to 5 L/min and one D to 50 cm^3/min (Tylan Corporation, 23301-TS Wilmington Ave., Carson, CA, 90745, Model 2160, or equivalent).

7.4.4 Teflon® filter(s) - 47-mm Teflon® filter for particulate control, best source.

8.0 Reagents and Materials

8.1 Gas cylinders of helium, hydrogen, nitrogen, and zero air - ultrahigh purity grade, best source.

8.2 Gas calibration standards - cylinder(s) containing approximately 10 ppmv of each of the following compounds of interest:

vinyl chloride	chlorobenzene
vinylidene chloride	benzyl chloride
1,1,2-trichloro-1,2,2-trifluoroethane	hexachloro-1,3-butadiene
chloroform	methyl chloroform
1,2-dichloroethane	carbon tetrachloride
benzene	trichloroethylene
toluene	cis-1,3-dichloropropene
Freon 12	trans-1,3-dichloropropene
methyl chloride	ethylbenzene
1,2-dichloro-1,1,2,2-tetrafluoroethane	o-xylene
methyl bromide	m-xylene
ethyl chloride	p-xylene
Freon 11	styrene
dichloromethane	1,1,2,2-tetrachloroethane
1,1-dichloroethane	1,3,5-trimethylbenzene
cis-1,2-dichloroethylene	1,2,4-trimethylbenzene
1,2-dichloropropane	m-dichlorobenzene
1,1,2-trichloroethane	o-dichlorobenzene
1,2-dibromoethane	p-dichlorobenzene
tetrachloroethylene	1,2,4-trichlorobenzene

The cylinder(s) should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA approved Certified Reference Material (CRM). The components may be purchased in one cylinder or may be separated into different cylinders. Refer to manufacturer's specification for guidance on purchasing and mixing VDCs in gas cylinders. Those compounds purchased should match one's own target list.

8.3 Cryogen - liquid oxygen (bp -183.0°C), or liquid argon (bp -185.7°C), best source.

8.4 Gas purifiers - connected in-line between hydrogen, nitrogen, and zero air gas cylinders and system inlet line, to remove moisture and organic impurities from gas streams (Alltech Associates, 2051 Waukegan Road, Deerfield, IL, 60015, or equivalent).

8.5 Deionized water - high performance liquid chromatography (HPLC) grade, ultrahigh purity (for humidifier), best source.

8.6 4-bromofluorobenzene - used for tuning GC-MS, best source.

8.7 Hexane - for cleaning sampling system components, reagent grade, best source.

8.8 Methanol - for cleaning sampling system components, reagent grade, best source.

9.0 Sampling System

9.1 System Description

9.1.1 Subatmospheric Pressure Sampling [See Figure 2 (Without Metal Bellows Type Pump)]

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg. When opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

9.1.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

9.1.2 Pressurized Sampling [See Figure 2 (With Metal Bellows Type Pump)]

9.1.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 103-206 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 cm^3/min for 24 hours to achieve a final pressure of about 144 kPa (21 psig).

9.1.2.2 In pressurized canister sampling, a metal bellows type pump draws in ambient air from the sampling manifold to fill and pressurize the sample canister.

9.1.3 All Samplers

9.1.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate (cm^3/min).
P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

where:

V = volume of the canister (cm^3).
T = sample period (hours).
For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by

$$F = \frac{2 \times 6000}{24 \times 60} 8.3 \text{ cm}^3\text{/min}$$

9.1.3.2 For automatic operation, the timer is wired to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and close the valve when stopping the pump.

9.1.3.3 The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 9(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 9(b).

9.1.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period. If a critical orifice is used, some drop in the flow rate may occur near the end of the sample period as the canister pressure approaches the final calculated pressure.

9.1.3.5 As an option, a second electronic timer (see Section 7.1.1.6) may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

9.1.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 12.2.2). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 12.1).

9.2 Sampling Procedure

9.2.1 The sample canister should be cleaned and tested according to the procedure in Section 12.1.

9.2.2 A sample collection system is assembled as shown in Figure 2 (and Figure 3) and must meet certification requirements as outlined in Section 12.2.3. [Note: The sampling system should be contained in an appropriate enclosure.]

9.2.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

9.2.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on canister sampling field data sheet (Figure 10). [Note: The following discussion is related to Figure 2.]

9.2.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system. [Note: For a subatmospheric sampler, the flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.] A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ± 10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected. [Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate, to compensate for any zero drift.] After two minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 cm^3/min for 24 hr, 7.0 cm^3/min for 12 hr). Record final flow under "CANISTER FLOW RATE," Figure 10.

9.2.6 The sampler is turned off and the elapsed time meter is reset to 000.0. Note: Any time the sampler is turned off, wait at least 30 seconds to turn the sampler back on.

9.2.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 12.1) canister is attached to the system.

9.2.8 The canister valve and vacuum/pressure gauge valve are opened.

9.2.9 Pressure/vacuum in the canister is recorded on the canister sampling field data sheet (Figure 10) as indicated by the sampler vacuum/pressure gauge.

9.2.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister sampling field data sheet.

9.2.11 The electronic timer is set to begin and stop the sampling period at the appropriate times. Sampling commences and stops by the programmed electronic timer.

9.2.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the sampling field data sheet. The current reading from the flow controller is recorded.

9.2.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the sampling field data sheet. Pressure should be close to desired pressure. [Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.] Time of day and elapsed time meter readings are also recorded.

9.2.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister sampling field data sheet (see Figure 10). [Note: For a pressurized system, the final flow may be measured directly.] The sampler is turned off.

9.2.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date are recorded on the tag.

10.0 Analytical System (See Figures 4, 5 and 6).

10.1 System Description

10.1.1 GC-MS-SCAN System

10.1.1.1 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode (see Figure 4). All ions are scanned by the MS repeatedly during the GC run. The system includes a computer and appropriate software for data acquisition, data reduction, and data reporting. A 400 cm^3 air sample is collected from the canister into the analytical system. The sample air is first passed through a Nafion® dryer, through the 6-port chromatographic valve, then routed into a cryogenic trap. [Note: While the GC-multidetector analytical system does not employ a Nafion® dryer for drying the sample gas stream, it is used here because the GC-MS system utilizes a larger sample volume and is far more sensitive to excessive moisture than the GC-multidetector analytical system. Moisture can adversely affect detector precision. The Nafion® dryer also prevents freezing of moisture on the 0.32 mm 1.0. column, which may cause column blockage and possible breakage.] The trap is heated (-160°C to 120°C in 60 sec) and the analyte is injected onto the OV-1 capillary column (0.32 mm x 50 m). [Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.] Upon sample injection onto the column, the MS computer is signaled by the GC computer to begin detection of compounds which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range should be 18 to 250 amu, resulting in a 1.5 Hz repetition rate. Six (6) scans per eluting chromatographic peak are provided at this rate. The 10-15 largest peaks are chosen by an automated data reduction program, the three scans nearest the peak apex are averaged, and a background subtraction is performed. A library search is then performed and the top ten best matches for each peak are listed. A qualitative characterization of the sample is provided by this procedure. A typical chromatogram of VOCs determined by GC-MS-SCAN is illustrated in Figure 11(a).

10.1.1.2 A Nafion® permeable membrane dryer is used to remove water vapor selectively from the sample stream. The permeable membrane consists of Nafion® tubing (a copolymer of tetrafluoroethylene and fluorosulfonyl monomer) that is coaxially mounted within larger tubing. The sample stream is passed through the interior of the Nafion® tubing, allowing water (and other light, polar compounds) to permeate through the walls into a dry air purge stream flowing through the annular space between the Nafion® and outer tubing. [Note: To prevent excessive moisture build-up and any memory effects in the dryer, a clean-up procedure involving periodic heating of the dryer (100°C for 20 minutes) while purging with dry zero air (500 cm^3/min) should be implemented as part of the user's SOP manual. The clean-up procedure is repeated during each analysis (see Section 14, reference 7). Recent studies have indicated no substantial loss of targeted VOCs utilizing the above clean-up procedure (7). This cleanup procedure is particularly useful when employing cryogenic preconcentration of VOCs with subsequent GC analysis using a 0.32 mm 1.0. column because excess accumulated water can cause trap and column blockage and also adversely affect detector precision. In addition, the improvement in water removal from the sampling stream will allow analyses of much larger volumes of sample air in the event that greater system sensitivity is required for targeted compounds.]

10.1.1.3 The packed metal tubing used for reduced temperature trapping of VOCs is shown in Figure 12. The cooling unit is comprised of a 0.32 cm outside diameter (O.D.) nickel tubing loop packed with 60-80 mesh Pyrex® beads (Nutech Model 320-01, or equivalent). The nickel tubing loop is wound onto a cylindrically formed tube heater (250 watt). A cartridge heater (25 watt) is sandwiched between pieces of aluminum plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. During operation, the trap is inside a two-section stainless steel shell which is well insulated. Rapid heating (-150 to +100°C in 55 s) is accomplished by direct thermal contact between the heater and the trap tubing. Cooling is achieved by vaporization of the cryogen. In the shell, efficient cooling (+120 to -150°C in 225 s) is facilitated by confining the vaporized cryogen to the small open volume surrounding the trap assembly. The trap assembly and chromatographic valve are mounted on a baseplate fitted into the injection and auxiliary zones of the GC on an insulated pad directly above the column oven when used with the Hewlett-Packard 5880 GC. [Note: Alternative trap assembly and connection to the GC may be used depending upon user's requirements.] The carrier gas line is connected to the injection end of the analytical column with a zero-dead-volume fitting that is usually held in the heated zone above the GC oven. A 15 cm x 15 cm x 24 cm aluminum box is fitted over the sample handling elements to complete the package. Vaporized cryogen is vented through the top of the box.

10.1.1.4 As an option, the analyst may wish to split the gas stream exiting the column with a low dead-volume tee, passing one-third of the sample gas (1.0 mL/min) to the mass-selective detector and the remaining two-thirds (2.0 mL/min) through a flame ionization detector, as illustrated as an option in Figure 4. The use of the specific detector (MS-SCAN) coupled with the non-specific detector (FID) enables enhancement of data acquired from a single analysis. In particular, the FID provides the user:

- Semi-real time picture of the progress of the analytical scheme;
- Confirmation by the concurrent MS analysis of other labs that can provide only FID results; and
- Ability to compare GC-FID with other analytical laboratories with only GC-FID capability.

10.1.2 GC-MS-SIM System

10.1.2.1 The analytical system is comprised of a GC equipped with an OV-1 capillary column (0.32 mm x 50 m) and a mass-selective detector set in the SIM mode (see Figure 4). The GC-MS is set up for automatic, repetitive analysis. The system is programmed to acquire data for only the target compounds and to disregard all others. The sensitivity is 0.1 ppbv for a 250 cm^3 air sample with analytical precision of about 5% relative standard deviation. Concentration of compounds based upon a previously installed calibration table is reported by an automated data reduction program. A Nafion® dryer is also employed by this analytical system prior to cryogenic preconcentration; therefore, many polar compounds are not identified by this procedure.

10.1.2.2 SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be ±0.10 minute of the library retention time of the compound. The acceptance level for relative abundance is determined to be ±15% of the expected abundance, except for vinyl chloride and methylene chloride, which is determined to be ±25%. Three ions are measured for most of the forty compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All the data should be manually examined by the analyst to determine the reason for the flag and whether the compound should be reported as found. While this adds some subjective judgment to the analysis, computer-generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range. A typical chromatogram of VOCs determined by GC-MS-SIM mode is illustrated in Figure 11(b).

10.1.3 GC-Multidetector (GC-FID-ECD) System with Optional PID

10.1.3.1 The analytical system (see Figure 5) is comprised of a gas chromatograph equipped with a capillary column and electron capture and flame ionization detectors (see Figure 5). In typical operation, sample air from pressurized canisters is vented past the inlet to the analytical system from the canister at a flow rate of 75 cm^3/min. For analysis, only 35 cm^3/min of sample gas is used, while excess is vented to the atmosphere. Sub-ambient pressure canisters are connected directly to the inlet. The sample gas stream is routed through a six port chromatographic valve and into the cryogenic trap for a total sample volume of 490 cm^3. [Note: This represents a 14 minute sampling period at a rate of 35 cm^3/min.] The trap (see Section 10.1.1.3) is cooled to -150°C by controlled release of a cryogen. VOCs and SVOCs are condensed on the trap surface while N_2, 0_2, and other sample components are passed to the pump. After the organic compounds are concentrated, the valve is switched and the trap is heated. The revolatilized compounds are transported by helium carrier gas at a rate of 4 cm^3/min to the head of the Megabore® OV-1 capillary column (0.53 mm x 30 m). Since the column initial temperature is at -50°C, the VOCs and SVOCs are cryofocussed on the head of the column. Then, the oven temperature is programmed to increase and the VOCs/SVOCs in the carrier gas are chromatographically separated. The carrier gas containing the separated VOCs/SVOCs is then directed to two parallel detectors at a flow rate of 2 cm^3/min each. The detectors sense the presence of the speciated VOCs/SVOCs, and the response is recorded by either a strip chart recorder or a data processing unit.

10.1.3.2 Typical chromatograms of VOCs determined by the GC-FID-ECD analytical system are illustrated in Figures 11(c) and 11(d), respectively.

10.1.3.3 Helium is used as the carrier gas (4 cm^3/min) to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs through the Megabore® GC column. Moisture and organic impurities are removed from the helium gas stream by a chemical purifier installed in the GC (see Section 7.2.1.11). After exiting the OV-1 Megabore® column, the carrier gas stream is split to the two detectors at rates of 2 cm^3/min each.

10.1.3.4 Gas scrubbers containing Drierite® or silica gel and 5A molecular sieve are used to remove moisture and organic impurities from the zero air, hydrogen, and nitrogen gas streams. [Note: Purity of gas purifiers is checked prior to use by passing humid zero-air through the gas purifier and analyzing according to Section 12.2.2.]

10.1.3.5 All lines should be kept as short as practical. All tubing used for the system should be chromatographic grade stainless steel connected with stainless steel fittings. After assembly, the system should be checked for leaks according to manufacturer's specifications.

10.1.3.6 The FID burner air, hydrogen, nitrogen (make-up), and helium (carrier) flow rates should be set according to the manufacturer's instructions to obtain an optimal FID response while maintaining a stable flame throughout the analysis. Typical flow rates are: burner air, 450 cm^3/min; hydrogen, 30 cm^3/min; nitrogen, 30 cm^3/min; helium, 2 cm^3/min.

10.1.3.7 The ECD nitrogen make-up gas and helium carrier flow rates should be set according to manufacturer's instructions to obtain an optimal ECD response. Typical flow rates are: nitrogen, 76 cm^3/min and helium, 2 cm^3/min.

10.1.3.8 The GC-FID-ECD could be modified to include a PID (see Figure 6) for increased sensitivity (20). In the photoionization process, a molecule is ionized by ultraviolet light as follows: R + hv — >R + e-, where R+ is the ionized species and a photon is represented by hv, with energy less than or equal to the ionization potential of the molecule. Generally all species with an ionization potential less than the ionization energy of the lamp are detected. Because the ionization potential of all major components of air (O_2, N_2, CO, CO_2, and H_2O) is greater than the ionization energy of lamps in general use, they are not detected. The sensor is comprised of an argon-filled, ultraviolet (UV) light source where a portion of the organic vapors are ionized in the gas stream. A pair of electrodes are contained in a chamber adjacent to the sensor. When a positive potential is applied to the electrodes, any ions formed by the absorption of UV light are driven by the created electronic field to the cathode, and the current (proportional to the organic vapor concentration) is measured. The PID is generally used for compounds having ionization potentials

less than the ratings of the ultraviolet lamps. This detector is used for determination of most chlorinated and oxygenated hydrocarbons, aromatic compounds, and high molecular weight aliphatic compounds. Because the PID is insensitive to methane, ethane, carbon monoxide, carbon dioxide, and water vapor, it is an excellent detector. The electron volt rating is applied specifically to the wavelength of the most intense emission line of the lamp's output spectrum. Some compounds with ionization potentials above the lamp rating can still be detected due to the presence of small quantities of more intense light. A typical system configuration associated with the GC-FID-ECD-PID is illustrated in Figure 6. This system is currently being used in EPA's FY-88 Urban Air Toxics Monitoring Program.

10.2 GC-MS-SCAN-SIM System Performance Criteria

10.2.1 GC-MS System Operation

10.2.1.1 Prior to analysis, the GC-MS system is assembled and checked according to manufacturer's instructions.

10.2.1.2 Table 3.0 outlines general operating conditions for the GC-MS-SCAN-SIM system with optional FID.

10.2.1.3 The GC-MS system is first challenged with humid zero air (see Section 11.2.2).

10.2.1.4 The GC-MS and optional FID system is acceptable if it contains less than 0.2 ppbv of targeted VOCs.

10.2.2 Daily GC-MS Tuning (See Figure 13)

10.2.2.1 At the beginning of each day or prior to a calibration, the GC-MS system must be tuned to verify that acceptable performance criteria are achieved.

10.2.2.2 For tuning the GC-MS, a cylinder containing 4-bromofluorobenzene is introduced via a sample loop valve injection system. [Note: Some systems allow auto-tuning to facilitate this process.] The key ions and ion abundance criteria that must be met are illustrated in Table 4. Analysis should not begin until all those criteria are met.

10.2.2.3 The GC-MS tuning standard could also be used to assess GC column performance (chromatographic check) and as an internal standard. Obtain a background correction mass spectra of 4-bromofluorobenzene and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

10.2.2.4 The performance criteria must be achieved before any samples, blanks or standards are analyzed. If any key ion abundance observed for the daily 4-bromofluorobenzene mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration gases reanalyzed until the above condition is met.

10.2.3 GC-MS Calibration (See Figure 13)

[Note: Initial and routine calibration procedures are illustrated in Figure 13.]

10.2.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-MS system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinder(s) are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2-L/min humidified zero air gas stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for a minimum of 30 minutes. After the equilibration period, the gas standard mixture is sampled and analyzed by the real-time GC-MS system [see Figure 8(a) and Section 7.2.1]. The results of the analyses are averaged, flow audits are performed on the mass flow meters and the calculated concentration compared to generated values. After the GC-MS is calibrated at three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC-MS system is certified clean (less than 0.2 ppbv of target compounds).

10.2.3.2 As an alternative a multipoint humid static calibration (three levels plus zero humid air) can be performed on the GC-MS system. During the humid static calibration analyses, three (3) SUMMA® passivated canisters are filled each at a different concentration between 1-20 ppbv from the calibration manifold using a pump and mass flow control arrangement [see Figure 8(c)]. The canisters are then delivered to the GC-MS to serve as calibration standards. The canisters are analyzed by the MS in the SIM mode, each analyzed twice. The expected retention time and ion abundance (see Table 2 and Table 5) are used to verify proper operation of the GC-MS system. A calibration response factor is determined for each analyte, as illustrated in Table 5, and the computer calibration table is updated with this information, as illustrated in Table 6.

10.2.3.3 Routine Calibration - The GC-MS system is calibrated daily (and before sample analysis) with a one-point calibration. The GC-MS system is calibrated either with the dynamic calibration procedure [see Figure 8(a)] or with a 6-L SUMMA® passivated canister filled with humid calibration standards from the calibration manifold (see Section 10.2.3.2). After the single point calibration, the GC-MS analytical system is challenged with a humidified zero gas stream to insure the analytical system returns to specification (less than 0.2 ppbv of selective organics).

10.3 GC-FID-ECD System Performance Criteria (With Optional PID System) (See Figure 14)

10.3.1 Humid Zero Air Certification

10.3.1.1 Before system calibration and sample analysis, the GC-FID-ECD analytical system is assembled and checked according to manufacturer's instructions.

10.3.1.2 The GC-FID-ECD system is first challenged with humid zero air (see Section 12.2.2) and monitored.

10.3.1.3 Analytical systems contaminated with less than 0.2 ppbv of targeted VOCs are acceptable.

10.3.2 GC Retention Time Windows Determination (See Table 7)

10.3.2.1 Before analysis can be performed, the retention time windows must be established for each analyte.

10.3.2.2 Make sure the GC system is within optimum operating conditions.

10.3.2.3 Make three injections of the standard containing all compounds for retention time window determination. [Note: The retention time window must be established for each analyte every 72 hours during continuous operation.]

10.3.2.4 Calculate the standard deviation of the three absolute retention times for each single component standard. The retention window is defined as the mean plus or minus three times the standard deviation of the individual retention times for each standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a closely-eluting, similar compound to develop a valid retention time window.

10.3.2.5 The laboratory must calculate retention time windows for each standard (see Table 7) on each GC column, whenever a new GC column is installed or when major components of the GC are changed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

10.3.3 GC Calibration

[Note: Initial and routine calibration procedures are illustrated in Figure 14.]

10.3.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-FID-ECD system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinders are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2-L/min humidified zero air stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for an appropriate amount of time. After

the equilibration period, the gas standard mixture is sampled and analyzed by the GC-MS system [see Figure 8(a)]. The results of the analyses are averaged, flow audits are performed on the mass flow controllers used to generate the standards and the appropriate response factors (concentration/area counts) are calculated for each compound, as illustrated in Table 5. [Note: GC-FIDs are linear in the 1-20 ppbv range and may not require repeated multipoint calibrations; whereas, the GC-ECD will require frequent linearity evaluation.] Table 5 outlines typical calibration response factors and retention times for 40 VOCs. After the GC-FID-ECD is calibrated at the three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC-FID-ECD system is certified clean (less than 0.2 ppbv of target compounds).

10.3.3.2 Routine Calibration - A one point calibration is performed daily on the analytical system to verify the initial multipoint calibration (see Section 10.3.3.1). The analyzers (GC-FID-ECD) are calibrated (before sample analysis) using the static calibration procedures (see Section 10.2.3.2) involving pressurized gas cylinders containing low concentrations of the targeted VOCs (10 ppbv) in nitrogen. After calibration, humid zero air is once again passed through the analytical system to verify residual VOCs are not present.

10.3.4 GC-FID-ECD-PID System Performance Criteria

10.3.4.1 As an option, the user may wish to include a photoionization detector (PID) to assist in peak identification and increase sensitivity.

10.3.4.2 This analytical system is presently being used in U.S. Environmental Protection Agency's Urban Air Toxic Pollutant Program (UATP).

10.3.4.3 Preparation of the GC-FID-ECD-PID analytical system is identical to the GC-FID-ECD system (see Section 10.3).

10.3.4.4 Table 8 outlines typical retention times (minutes) for selected organics using the GC-FID-ECD-PID analytical system.

10.4 Analytical Procedures

10.4.1 Canister Receipt

10.4.1.1 The overall condition of each sample canister is observed. Each canister should be received with an attached sample identification tag.

10.4.1.2 Each canister is recorded in the dedicated laboratory logbook. Also noted on the identification tag are date received and initials of recipient.

10.4.1.3 The pressure of the canister is checked by attaching a pressure gauge to the canister inlet. The canister valve is opened briefly and the pressure (kPa, psig) is recorded. [Note: If pressure is <83 kPa (<12 psig), the user may wish to pressurize the canisters, as an option, with zero grade nitrogen up to 137 kPa (20 psig) to ensure that enough sample is available for analysis. However, pressurizing the canister can introduce additional error, increase the minimum detection limit (MDL), and is time consuming. The user should weigh these limitations as part of his program objectives before pressurizing.] Final cylinder pressure is recorded on canister sampling field data sheet (see Figure 10).

10.4.1.4 If the canister pressure is increased, a dilution factor (DF) is calculated and recorded on the sampling data sheet.

$$DF = \frac{Y_a}{X_a}$$

where:

X_a = canister pressure (kPa, psia) absolute before dilution.
Y_a = canister pressure (kPa, psia) absolute after dilution.

After sample analysis, detected VOC concentrations are multiplied by the dilution factor to determine concentration in the sampled air.

10.4.2 GC-MS-SCAN Analysis (With Optional FID System)

10.4.2.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.3), operated (see Table 3), and calibrated for accurate VOC determination.

10.4.2.2 The mass flow controllers are cheched and adjusted to provide correct flow rates for the system.

10.4.2.3 The sample canister is connected to the inlet of the GC-MS-SCAN (with optional FID) analytical system. For pressurized samples, a mass flow controller is placed on the canister and the canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at a flow of 75 cm^3/min so that 40 cm^3/min is pulled through the Mafion® dryer to the six-port chromatographic valve. [Note: Flow rate is not as important as acquiring sufficient sample volume.] Sub-ambient pressure samples are connected directly to the inlet.

10.4.2.4 The GC oven and cryogenic trap (inject position) are cooled to their set points of -50°C and -160°C, respectively.

10.4.2.5 As soon as the cryogenic trap reaches its lower set point of -160°C, the six-port chromatographic valve is turned to its fill position to initiate sample collection.

10.4.2.6 A ten minute collection period of canister sample is utilized. (Note: 40 cm^3/min x 10 min = 400 cm^3 sampled canister contents.]

10.4.2.7 After the sample is preconcentrated in the cryogenic trap, the GC sampling valve is cycled to the inject position and the cryogenic trap is heated. The trapped analytes are thermally desorbed onto the head of the OV-1 capillary column (0.31 mm 1.0. x 50 m length). The GC oven is programmed to start at -50°C and after 2 min to heat to 150°C at a rate of 8°C per minute.

10.4.2.8 Upon sample injection onto the column, the MS is signaled by the computer to scan the eluting carrier gas from 18 to 250 amu, resulting in a 1.5 Hz repetition rate. This corresponds to about 6 scans per eluting chromatographic peak.

10.4.2.9 Primary identification is based upon retention time and relative abundance of eluting ions as compared to the spectral library stored on the hard disk of the GC-MS data computer.

10.4.2.10 The concentration (ppbv) is calculated using the previously established response factors (see Section 10.2.3.2), as illustrated in Table 5. [Note: If the canister is diluted before analysis, an appropriate multiplier is applied to correct for the volume dilution of the canister (Section 10.4.1.4).]

10.4.2.11 The optional FID trace allows the analyst to record the progress of the analysis.

10.4.3 GC-MS-SIM Analysis (With Optional FID System)

10.4.3.1 When the MS is placed in the SIM mode of operation, the MS monitors only preselected ions, rather than scanning all masses continuously between two mass limits.

10.4.3.2 As a result, increased sensitivity and improved quantitative analysis can be achieved.

10.4.3.3 Similar to the GC-MS-SCAN configuration, the GC-MS-SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2 and Table 5). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic Peak. Once the GC-MS-SIM has identified the peak, a calibration response factor is used to determine the analyte's concentration.

10.4.3.4 The individual analyses are handled in three phases: data acquisition, data reduction, and data reporting. The data acquisition software is set in the SIM mode, where specific compound fragments are monitored by the MS at specific times in the analytical rum. Data reduction is coordinated by the postprocessing macro program that is automatically accessed after data acquisition is completed at the end of the GC run. Resulting ion profiles are extracted, peaks are identified and integrated, and an internal integration report is generated by the program. A reconstructed ion chromatogram for hardcopy reference is prepared by the program and various parameters of interest such as time, date, and integration constants are printed. At the completion of the macro program, the data reporting software is accessed. The appropriate calibration table (see Table 9) is retrieved by the data reporting program

from the computer's hard disk storage and the proper retention time and response factor parameters are applied to the macro program's integration file. With reference to certain pre-set acceptance criteria, peaks are automatically identified and quantified and a final summary report is prepared, as illustrated in Table 10.

10.4.4 GC-FID-ECD Analysis (With Optional PID System)

10.4.4.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.2) and calibrated through a dynamic standard calibration procedure (see Section 10.3.2). The FID detector is lit and allowed to stabilize.

10.4.1.2 Sixty-four minutes are required for each sample analysis - 15 min for system initialization, 14 min for sample collection, 30 min for analysis, and 5 min for post-time, during which a report is printed. [Note: This may vary depending upon system configuration and programming.]

10.4.4.3 The helium and sample mass flow controllers are checked and adjusted to provide correct flow rates for the system. Helium is used to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs from the trap onto the GC column and into the FID-ECD. The hydrogen, burner air, and nitrogen flow rates should also be checked. The cryogenic trap is connected and verified to bc operating properly while flowing cryogen through the system.

10.4.4.4 The sample canister is connected to the inlet of the GC-FID-ECD analytical system. The canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at 75 cm^3/min using a 0-500 cm^3/min Tylan mass flow controller. During analysis, 40 cm^3/min of sample gas is pulled through the six-port chromatographic valve and routed through the trap at the appropriate time while the extra sample is vented. The VOCs are condensed in the trap while the excess flow is exhausted through an exhaust vent, which assures that the sample air flowing through the trap is at atmospheric pressure.

10.4.4.5 The six-port valve is switched to the inject position and the canister valve is closed.

10.4.4.6 The electronic integrator is started.

10.4.4.7 After the sample is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the columm is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs elute from the column to the parallel FID-ECD assembly.

10.4.4.8 The peaks eluting from the detectors are identified by retention time (see Table 7 and Table 8), while peak areas are recorded in area counts. Figures 15 and 16 illustrate typical response of the FID and ECD, respectively, for the forty (40) targeted VOCs. [Note: Refer to Table 7 for peak number and identification.]

10.4.4.9 The response factors (see Section 10.3.3.1) are multiplied by the area counts for each peak to calculate ppbv estimates for the unknown sample. If the canister is diluted before analysis, an appropriate dilution multiplier (DF) is applied to correct for the volume dilution of the canister (see Section 10.4.1.4).

10.4.4.10 Depending on the number of canisters to be analyzed, each canister is analyzed twice and the final concentrations for each analyte are the averages of the two analyses.

10.4.4.11 However, if the GC-FID-ECD analytical system discovers unexpected peaks which need further identification and attention or overlapping peaks are discovered, eliminating possible quantitation, the sample should then be subjected to a GC-MS-SCAN for positive identification and quantitation.

11.0 Cleaning and Certification Program

11.1 Canister Cleaning and Certification

11.1.1 All canisters must be clean and free of any contaminants before sample collection.

11.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air. [Note: The canister cleaning system in Figure 7 can be used for this task.] The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If leak tight, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

11.1.3 A canister cleaning system may be assembled as illustrated in Figure 7. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to < 0.05 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

11.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

11.1.5 The zero shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Steps 11.1.3 through 11.1.5 are repeated two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

11.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC-MS or GC-FID-ECD analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of targets VOCs). The check can then be reduced to a lower percentage of canisters.

11.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the neck of each canister for field notes and chain-of-custody purposes.

11.1.8 As an option to the humid zero air cleaning procedures, the canisters could be heated in an isothermal oven to 100°C during Section 11.1.3 to ensure that lower molecular weight compounds (C2-C8) are not retained on the walls of the canister. [Note: For sampling heavier, more complex VOC mixtures, the canisters should be heated to 250°C during Section 11.1.3.7.] Once heated, the canisters are evacuated to 0.05 mm Hg. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by the GC-FID-ECD system. Any canister that has not tested clean (less than 0.2 ppbv of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to 0.05 mm Hg and remain in the evacuated state until used.

11.2 Sampling System Cleaning and Certification

11.2.1 Cleaning Sampling System Components

11.2.1.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

11.2.1.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

11.2.1.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

11.2.2 Humid Zero Air Certification

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv of targeted compounds) have occurred when challenged with the test gas stream.]

11.2.2.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas cylinder, as follows.

11.2.2.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas cylinder) is connected to the manifold and the zero air cylinder activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

11.2.2.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to a GC-FID-ECD analytical system at 75 cm^3/min so that 40 cm^3/min is pulled through the six-port valve and routed through the cryogenic trap (see Section 10.2.2.1) at the appropriate time while the extra sample is vented. [Note: The exit of the sampling system (without the canister) replaces the canister in Figure 4.] After the sample (400 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC-MS (see Section 10.2) or the GC-FID-ECD (see Section 10.3). The analytical system should not detect greater than 0.2 ppbv of targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms of a certified sampler and contaminated sampler are illustrated in Figures 17(A) and (b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 11.2.3.

11.2.3 Sampler System Certification with Humid Calibration Gas Standards

11.2.3.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

11.2.3.2 Verify that the calibration system is clean (less than 0.2 ppbv of targeted compounds) by sampling a humidified gas stream, without gas calibration standards, with a previously certified clean canister (see Section 12.1).

11.2.3.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of targeted compounds are found.

11.2.3.4 For generating the humidified calibration standards, the calibration gas cylinder(s) (see Section 8.2) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs, are attached to the calibration system, as outlined in Section 10.2.3.1. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 cm^3/min certified mass flow controllers to generate ppb levels of calibration standards.

11.2.3.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(a).

11.2.3.6 Sample the dynamic calibration gas stream with the sampling system according to Section 9.2.1. [Note: To conserve generated calibration gas, bypass the canister sampling system manifold and attach the sampling system to the calibration gas stream at the inlet of the in-line filter of the sampling system so the flow will be less than 500 cm^3/min.]

11.2.3.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC-MS or GC-multidetector analytical system [Figure 8(b)] to provide reference concentrations of generated VOCs.

11.2.3.8 At the end of the sampling period (normally same time period used for anticipated sampling), the sampling system canister is analyzed and compared to the reference GC-MS or GC-multidetector analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

11.2 3.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

12.0 Performance Criteria and Quality Assurance

12.1 Standard Operating Procedures (SOPs)

12.1.1 SOPs should be generated in each laboratory describing and documenting the following activities: (1) assembly, calibration, leak check, and operation of specific sampling systems and equipment used; (2) preparation, storage, shipment, and handling of samples; (3) assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used; (4) canister storage and cleaning; and (5) all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the laboratory personnel conducting the work.

12.2 Method Relative Accuracy and Linearity

12.2.1 Accuracy can be determined by injecting VOC standards (see Section 8.2) from an audit cylinder into a sampler. The contents are then analyzed for the components contained in the audit canister. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = \frac{X - Y}{X} \times 100$$

Where: Y = Concentration of the targeted compound recovered from sampler.

X = Concentration of VOC targeted compound in the NBS-SRM or EPA-CRM audit cylinders.

12.2.2 If the relative accuracy does not fall between 90 and 110 percent, the field sampler should be removed from use, cleaned, and recertified according to initial certification procedures outlined in Section 11.2.2 and Section 11.2.3. Historically, concentrations of carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene have sometimes been detected at lower concentrations when using parallel ECD and FID detectors. When these three compounds are present at concentrations close to calibration levels, both detectors usually agree on the reported concentrations. At concentrations below 4 ppbv, there is a problem with nonlinearity of the ECD. Plots of concentration versus peak area for calibration compounds detected by the ECD have shown that the curves are nonlinear for carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene, as illustrated in Figures 18(a) through 18(c). Other targeted ECD and FID compounds scaled linearly for the range 0 to 8 ppbv, as shown for chloroform in Figure 18(d). For compounds that are not linear over the calibration range, area counts generally roll off between 3 and 4 ppbv. To correct for the nonlinearity of these compounds, an additional calibration step is performed. An evacuated stainless steel canister is pressurized with calibration gas at a nominal concentration of 8 ppbv. The sample is then diluted to approximately 3.5 ppbv with zero air and analyzed. The instrument response factor (ppbv/area) of the ECD for each of the three compounds is calculated for the 3.5 ppbv sample. Then, both the 3.5 ppbv and the 8 ppbv response factors are entered into the ECD calibration table. The software for the Hewlett-Packard 5880 level 4 GC is designed to accommodate multilevel calibration entries, so the correct response factors are automatically calculated for concentrations in this range.

12.3 Method Modification

12.3.1 Sampling

12.3.1.1 The sampling system for pressurized canister sampling could be modified to use a lighter, more compact pump. The pump currently being used weighs about 16 kilograms (35 lbs). Commercially available pumps that could be used as alternatives to the prescribed sampler pump are described below. Metal Bellows MB-41 pump: These pumps are cleaned at the factory; however, some precaution should be taken with the circular (4.8 cm diameter) Teflon® and stainless steel part directly under the flange. It is often dirty when received and should be cleaned before use. This part is cleaned by removing it from the pump, manually cleaning with deionized water, and placing in a vacuum oven at 100°C for at least 12 hours. Exposed parts of the pump head are also cleaned with swabs and allowed to air dry. These pumps have proven to be very reliable; however, they are only useful up to an outlet pressure of about 137 kPa (20 psig). Neuberger Pump: Viton gaskets or seals must be specified with this pump. The "factory direct" pump is received contaminated and leaky. The pump is cleaned by disassembling the pump head (which consists of

three stainless steel parts and two gaskets), cleaning the gaskets with deionized water and drying in a vacuum oven, and remachining (or manually lapping) the sealing surfaces of the stainless steel parts. The stainless steel parts are then cleaned with methanol, hexane, deionized water and heated in a vacuum oven. The cause for most of the problems with this pump has been scratches on the metal parts of the pump head. Once this rework procedure is performed, the pump is considered clean and can be used up to about 240 kPa (35 psig) output pressure. This pump is utilized in the sampling system illustrated in Figure 3.

12.3.1.2 Urban Air Toxics Sampler

The sampling system described in this method can be modified like the sampler in EPA's FY-88 Urban Air Toxics Pollutant Program. This particular sampler is described in Appendix C (see Figure 19).

12.3.2 Analysis

12.3.2.1 Inlet tubing from the calibration manifold could be heated to 50°C (same temperature as the calibration manifold) to prevent condensation on the internal walls of the system.

12.3.2.2 The analytical strategy for Method TO-14 involves positive identification and quantitation by GC-MS-SCAN-SIM mode of operation with optional FID. This is a highly specific and sensitive detection technique. Because a specific detector system (GC-MS-SCAN-SIM) is more complicated and expensive than the use of non-specific detectors (GC-FID-ECD-PID), the analyst may want to perform a screening analysis and preliminary quantitation of VOC species in the sample, including any polar compounds, by utilizing the GC-multidetector (GC-FID-ECD-PID) analytical system prior to GC-MS analysis. This system can be used for approximate quantitation. The GC-FID-ECD-PID provides a "snap-shot" of the constituents in the sample, allowing the analyst to determine:

- Extent of misidentification due to overlapping peaks,
- Whether the constituents are within the calibration range of the anticipated GC-MS-SCAN-SIM analysis or does the sample require further dilution, and
- Are there unexpected peaks which need further identification through GC-MS-SCAN or are there peaks of interest needing attention?

If unusual peaks are observed from the GC-FID-ECD-PID system, the analyst then performs a GC-MS-SCAN analysis. The GC-MS-SCAN will provide positive identification of suspect peaks from the GC-FID-ECD-PID system. If no unusual peaks are identified and only a select number of VOCs are of concern, the analyst can then proceed to GC-MS-SIM. The GC-MS-SIM is used for final quantitation of selected VOCs. Polar compounds, however, cannot be identified by the GC-MS-SIM due to the use of a Nafion® dryer to remove water from the sample prior to analysis. The dryer removes polar compounds along with the water. The analyst often has to make this decision incorporating project objectives, detection limits, equipment availability, cost and personnel capability in developing an analytical strategy. Figure 20 outlines the use of the GC-FID-ECD-PID as a "screening" approach, with the GC-MS-SCAN-SIM for final identification and quantitation.

12.4 Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

12.5 Quality Assurance (See Figure 21)

12.5.1 Sampling System

12.5.1.1 Section 9.2 suggests that a portable GC system be used as a "screening analysis" prior to locating fixed-site samplers (pressurized or subatmospheric).

12.5.1.2 Section 9.2 requires pre and post-sampling measurements with a certified mass flow controller for flow verification of sampling system.

12.5.1.3 Section 11.1 requires all canisters to be pressure tested to 207 kPa ±14 kPa (30 psig ±2 psig) over a period of 24 hours.

12.5.1.4 Section 11.1 requires that all canisters be certified clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.5 Section 11.2.2 requires all field sampling systems to be certified initially clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.6 Section 11.2.3 requires all field sampling systems to pass an initial humidified calibration gas certification [at VOC concentration levels expected in the field (e.g., 0.5 to 2 ppbv)] with a percent recovery of greater than 90.

12.5.2 GC-MS-SCAN-SIM System Performance Criteria

12.5.2.1 Section 10.2.1 requires the GC-MS analytical system to be certified clean (less than 0.2 ppbv of targeted VOCs) prior to sample analysis, through a humid zero air certification.

12.5.2.2 Section 10.2.2 requires the daily tuning of the GC-MS with 4-bromofluorobenzene (4-BFB) and that it meet the key ions and ion abundance critera (10%) outlined in Table 5.

12.5.2.3 Section 10.2.3 requires both an initial multipoint humid static calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-MS analytical system.

12.5.3 GC-Multidetector System Performance Criteria

12.5.3.1 Section 10.3.1 requires the GC-FID-ECD analytical system, prior to analysis, to be certified clean (less than 0.2 ppbv of targeted VOCs) through a humid zero air certification.

12.5.3.2 Section 10.3.2 requires that the GC-FID-ECD analytical system establish retention time windows for each analyte prior to sample analysis, when a new GC column is installed, or major components of the GC system altered since the previous determination.

12.5.3.3 Section 8.2 requires that all calibration gases be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA approved Certified Reference Material (CRM).

12.5.3.4 Section 10.3.2 requires that the retention time window be established throughout the course of a 72-hr analytical period.

13.5.3.5 Section 10.3.3 requires both an initial multipoint calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-FID-ECD analytical system with zero gas dilution of NBS traceable or NBS/EPA CRMs gases. [Note: Gas cylinders of VOCs at the ppm and ppb level are available for audits from the USEPA, Environmental Monitoring Systems Laboratory, Quality Assurance Division, MD-77B, Research Triangle Park, NC 27711, (919)541-4531. Appendix A outlines five groups of audit gas cylinders available from USEPA.]

13.0 Acknowledgements

The determination of volatile and some semi-volatile organic compounds in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analytical procedures. While there are numerous procedures for sampling and analyzing VOCs/SVOCs in ambient air, this method draws upon the best aspects of each one and combines them into a standardized methodology. To that end, the following individuals contributed to the research, documentation and peer review of this manuscript.

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TABLE 1. VOLATILE ORGANIC COMPOUND DATA SHEET

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)	CAS NUMBER
Freon 12 (Dichlorodifluoromethane)	Cl_2CF_2	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH_3Cl	50.49	-24.2	-97.1	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	170.93	4.1	-94.0	
Vinyl chloride (Chloroethylene)	$CH_2 = CHCl$	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH_3Br	94.94	3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH_3CH_2Cl	64.52	12.3	-136.4	75-00-3
Freon 11 (Trichlorofluoromethane)	CCl_3F	137.38	23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	$C_2H_2Cl_2$	96.95	31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH_2Cl_2	84.94	39.8	-95.1	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	187.38	47.7	-36.4	
1,1-Dichloroethane (Ethylidene chloride)	CH_3CHCl_2	98.96	57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	$CHCl = CHCl$	96.94	60.3	-80.5	
Chloroform (Trichloromethane)	$CHCl_3$	119.38	61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	$ClCH_2CH_2Cl$	98.96	83.5	-35.3	107-6-2
Methyl chloroform (1,1,1-Trichloroethane)	CH_3CCl_3	133.41	74.1	-30.4	71-55-6
Benzene (Cyclohexatriene)	C_6H_6	78.12	80.1	5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl_4	153.82	76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	$CH_3CHClCH_2Cl$	112.99	96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	$ClCH = CCl_2$	131.29	87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$CH_3CCl = CHCl$	110.97	76		
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	$ClCH_2CH = CHCl$	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	$CH_2ClCHCl_2$	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	$C_6H_5CH_3$	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	$BrCH_2CH_2Br$	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	$Cl_2C = CCl_2$	165.83	121.1	-19.0	127-18-4
Chlorobenzene (Phenyl chloride)	C_6H_5Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	$C_6H_5C_2H_5$	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	$1,3\text{-}(CH_3)_2C_6H_4$	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	$1,4\text{-}(CH_3)_2C_6H_4$	106.17	138.3	13.3	
Styrene (Vinyl benzene)	$C_6H_5CH = CH_2$	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	$1,2\text{-}(CH_3)_2C_6H_4$	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5\text{-}(CH_3)_3C_6H_6$	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	$1,2,4\text{-}(CH_3)_3C_6H_6$	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3\text{-}Cl_2C_6H_4$	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	$C_6H_5CH_2Cl$	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	$1,2\text{-}Cl_2C_6H_4$	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4\text{-}Cl_2C_6H_4$	147.01	174.0	53.1	106.46.7
1,2,4-Trichlorobenzene	$1,2,4\text{-}Cl_3C_6H_3$	181.45	213.5	17.0	120-82-1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3,butadiene)					

TABLE 2. ION/ABUNDANCE AND EXPECTED RETENTION TIME FOR SELECTED VOCs ANALYZED BY GC-MS-SIM

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (min)
Freon 12 (Dichlorodifluoromethane)	85/100 87/ 31	5.01
Methyl chloride (Chloromethane)	50/100 52/ 34	5.69
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	85/100 135/ 56 87/ 33	6.55
Vinyl chloride (Chloroethene)	62/100 27/125 64/ 32	6.71
Methyl bromide (Bromomethane)	94/100 96/ 85	7.83
Ethyl chloride (Chloroethane)	64/100 29/140 27/140	8.43
Freon 11 (Trichlorofluoromethane)	101/100 103/ 67	9.97
Vinylidene chloride (1,1-Dichloroethylene)	61/100 96/ 55 63/ 31	10.93
Dichloromethane (Methylene chloride)	49/100 84/ 65 86/ 45	11.21
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	151/100 101/140 103/ 90	11.60
1,1-Dichloroethane (Ethylidene dichloride)	63/100 27/ 64 65/ 33	12.50
cis-1,2-Dichloroethylene	61/100 96/ 60 98/ 44	13.40
Chloroform (Trichloromethane)	83/100 85/ 65 47/ 35	13.75
1,2-Dichloroethane (Ethylene dichloride)	62/100 27/ 70 64/ 31	14.39
Methyl chloroform (1,1,1-Trichloroethane)	97/100 99/ 64 61/ 61	14.62
Benzene (Cyclohexatriene)	78/100 77/ 25 50/ 35	15.04
Carbon tetrachloride (Tetrachloromethane)	117/100 119/ 97	15.18
1,2-Dichloropropane (Propylene dichloride)	63/100 41/ 90 62/ 70	15.83
Trichloroethylene (Trichloroethene)	130/100 132/ 92 95/ 87	16.10
cis-1,3-Dichloropropene	75/100 39/ 70 77/ 30	16.96
trans-1,3-Dichloropropene (1,3-dichloro-1-propene)	75/100 39/ 70 77/ 30	17.49

(continued)

TABLE 2. ION/ABUNDANCE AND EXPECTED RETENTION TIME FOR SELECTED VOCs ANALYZED BY GC-MS-SIM (cont.)

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (min)
1,1,2-Trichloroethane (Vinyl trichloride)	97/100 83/ 90 61/ 82	17.61
Toluene (Methyl benzene)	91/100 92/ 57	17.86
1,2-Dibromoethane (Ethylene dibromide)	107/100 109/ 96 27/115	18.48
Tetrachloroethylene (Perchloroethylene)	166/100 164/ 74 131/ 60	19.01
Chlorobenzene (Benzene chloride)	112/100 77/ 62 114/ 32	19.73
Ethylbenzene	91/100 106/ 28	20.20
m,p-Xylene(1,3/1,4-dimethylbenzene)	91/100 106/ 40	20.41
Styrene (Vinyl benzene)	104/100 78/ 60 103/ 49	20.81
1,1,2,2-Tetrachloroethane (Tetrachloroethane)	83/100 85/ 64	20.92
o-Xylene (1,2-Dimethylbenzene)	91/100 106/ 40	20.92
4-Ethyltoluene	105/100 120/ 29	22.53
1,3,5-Trimethylbenzene (Mesitylene)	105/100 120/ 42	22.65
1,2,4-Trimethylbenzene (Pseudocumene)	105/100 120/ 42	23.18
m-Dichlorobenzene (1,3-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.31
Benzyl chloride (α-Chlorotoluene)	91/100 126/ 26	23.32
p-Dichlorobenzene (1,4-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.41
o-Dichlorobenzene (1,2-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.88
1,2,4-Trichlorobenzene	180/100 182/ 98 184/ 30	26.71
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	225/100 227/ 66 223/ 60	27.68

TABLE 3. GENERAL GC AND MS OPERATING CONDITIONS

Chromatography	
Column	Hewlett-Packard OV-1 crosslinked methyl silicone (50 m x 0.31-mm I.D., 17 um film thickness), or equivalent
Carrier Gas	Helium (2.0 cm3/min at 250°C)
Injection Volume	Constant (1-3 uL)
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	-50°C
Initial Hold Time	2 min
Program	8°C/min to 150°C
Final Hold Time	15 min
Mass Spectrometer	
Mass Range	18 to 250 amu
Scan Time	1 sec/scan
EI Condition	70 eV
Mass Scan	Follow manufacturer's instruction for selecting mass selective detector (MS) and selected ion monitoring (SIM) mode
Detector Mode	Multiple ion detection
FID System (Optional)	
Hydrogen Flow	30 cm^3/minute
Carrier Flow	30 cm^3/minute
Burner Air	400 cm^3/minute

TABLE 4. 4-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 5. RESPONSE FACTORS (ppbv/area count) AND EXPECTED RETENTION TIME FOR GC-MS-SIM ANALYTICAL CONFIGURATION

Compounds	Response Factor (ppbv/area count)	Expected Retention Time (minutes)
Freon 12	0.6705	5.01
Methyl chloride	4.093	5.64
Freon 114	0.4928	6.55
Vinyl chloride	2.343	6.71
Methyl bromide	2.647	7.83
Ethyl chloride	2.954	8.43
Freon 11	0.5145	9.87
Vinylidene chloride	1.037	10.93
Dichloromethane	2.255	11.21
Trichlorotrifluoroethane	0.9031	11.60
1,1-Dichloroethane	1.273	12.50
cis-1,2-Dichloroethylene	1.363	13.40
Chloroform	0.7911	13.75
1,2-Dichloroethane	1.017	14.39
Methyl chloroform	0.7078	14.62
Benzene	1.236	15.04
Carbon tetrachloride	0.5880	15.18
1,2-Dichloropropane	2.400	15.83
Trichloroethylene	1.383	16.10
cis-1,3-Dichloropropene	1.877	16.96
trans-1,3-Dichloropropene	1.338	17.49
1,1,2-Trichloroethane	1.891	17.61
Toluene	0.9406	17.86
1,2-Dibromoethane (EDB)	0.8662	18.48
Tetrachloroethylene	0.7357	19.01
Chlorobenzene	0.8558	19.73
Ethylbenzene	0.6243	20.20
m,p-Xylene	0.7367	20.41
Styrene	1.888	20.80
1,1,2,2-Tetrachloroethane	1.035	20.92
o-Xylene	0.7498	20.92
4-Ethyltoluene	0.6181	22.53
1,3,5-Trimethylbenzene	0.7088	22.65
1,2,4-Trimethylbenzene	0.7536	23.18
p-Dichlorobenzene	0.8912	23.41
1,2,4-Trimethylbenzene	0.7536	23.18
m-Dichlorobenzene	0.9643	23.31
Benzyl chloride	1.420	23.32
p-Dichlorobenzene	0.8912	23.41
o-Dichlorohenzene	1.004	23.88
1,2,4-Trichlorobenzene	2.150	26.71
Hexachlorobutadiene	0.4117	27.68

TABLE 6. GC-MS-SIM CALIBRATION TABLE

External Standard

Operator: JDP
Sample Info: SRY 1
Misc Info:
Integration File Name: DATA:SYR2A02A.I

8 Jan 87 10:02 am

Sequence Index: 1 Bottle Number 2:

Last Update: 8 Jan. 86 8:13 am
Reference Peak Window: 5:00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 Uncalibrated Peak RF: 0.00 Multiplier: 1.667

Peak Num.	Int Type	Ret Time	Signal Description		Compound Name	Area	Amount	
1	1 PP	5.020	Mass	85.00 amu	FREON 12	12893	4011	pptv
2	1 PP	5.654	Mass	50.00 amu	METHYLCHLORIDE	4445	2586	pptv
3	1 BP	6.525	Mass	85.00 amu	FREON 114	7067	1215	pptv
4	1 PB	6.650	Mass	62.00 amu	VINYLCHLORIDE	2892	1929	pptv
5	1 BP	7.818	Mass	94.00 amu	METHYLBROMIDE	2401	1729	pptv
6	1 BB	8.421	Mass	64.00 amu	ETHYLCHLORIDE	2134	2769	pptv
7	1 BV	9.940	Mass	101.00 amu	FREON 11	25069	6460	pptv
8	1 BP	10.869	Mass	61.00 amu	VINDENECHLOR	5034	1700	pptv
9	1 BP	11.187	Mass	49.00 amu	DICHLOROMETH	4803	2348	pptv
10	1 PP	11.223	Mass	41.00 amu	ALLYLCHLORID	761	8247	pptv
11	1 BP	11.578	Mass	151.00 amu	3CHL3FLUETHA	5477	1672	pptv
12	1 BP	12.492	Mass	63.00 amu	1,1DICHLOETH	5052	1728	pptv
13	1 VP	13.394	Mass	61.00 amu	c-1,2DICHLET	4761	1970	pptv
14	1 PH	13.713	Mass	83.00 amu	CHLOROFORM	5327	1678	pptv
15	1 BP	14.378	Mass	62.00 amu	1,2DICHLETHA	5009	2263	pptv
16	1 PB	14.594	Mass	97.00 amu	METHCHLOROFO	6656	2334	pptv
17	1 VP	15.009	Mass	78.00 amu	BENZENE	8332	2167	pptv
18	1 VP	15.154	Mass	117.00 amu	CARBONTETRAC	5888	1915	pptv
19	1 BB	15.821	Mass	63.00 amu	1,2DICHLPROP	3283	1799	pptv
20	1 BB	16.067	Mass	130.00 amu	TRICHLETHENE	4386	2109	pptv
21	1 PB	16.941	Mass	75.00 amu	c-1,3DICHLPR	2228	987.3	pptv
22	1 BP	17.475	Mass	75.00 amu	t-1,3DICHLPR	1626	689.2	pptv
23	1 BB	17.594	Mass	97.00 amu	1,1,2CHLRTHA	2721	1772	pptv
24	1 BV	17.844	Mass	91.00 amu	TOLUENE	14417	2733	pptv
25	1 PB	18.463	Mass	107.00 amu	EDB	4070	1365	pptv
26	1 PH	18.989	Mass	166.00 amu	TETRACHLETHE	6874	2065	pptv
27	1 PB	19.705	Mass	112.00 amu	CHLOROBENZEN	5648	1524	pptv
28	1 BP	20.168	Mass	91.00 amu	ETHYLBENZENE	11084	1842	pptv
29	1 PB	20.372	Mass	91.00 amu	m,p-XYLENE	17989	37909	pptv
30	1 BV	20.778	Mass	104.00 amu	STYRENE	3145	1695	pptv
31	1 BH	20.887	Mass	83.00 amu	TETRACHLETHA	4531	1376	pptv
32	1 BP	20.892	Mass	91.00 amu	o-XYLENE	9798	2010	pptv
33	1 VV	22.488	Mass	105.00 amu	4-ETHYLTOLUE	7694	14811	pptv
34	1 VB	22.609	Mass	105.00 amu	1,3,5METHBEN	6781	1705	pptv
35	1 BB	23.114	Mass	105.00 amu	1,2,4METHBEN	7892	2095	pptv
36	1 BV	23.273	Mass	146.00 amu	m-DICHLBENZE	3046	1119	pptv
37	1 VV	23.279	Mass	91.00 amu	BENZYLCHLORI	3880	1006	pptv
38	1 VB	23.378	Mass	146.00 amu	p-DICHLBENZE	6090	2164	pptv
39	1 BP	23.850	Mass	146.00 amu	o-DICHLBENZE	2896	1249	pptv
40	1 BB	26.673	Mass	180.00 amu	1,2,4CHLBENZ	562	767.1	pptv
41	1 BB	27.637	Mass	225.00 amu	HEXACHLBUTAD	6309	1789	pptv

TABLE 7. TYPICAL RETENTION TIME (MIN) AND CALIBRATION RESPONSE FACTORS (ppbv/area count) FOR TARGETED VOCs ASSOCIATED WITH FID AND ECD ANALYTICAL SYSTEM

Peak Number[1]	Compound	Retention Time (RT), minutes	FID Response Factor (RF) (ppbv/area count)	ECD Response Factor (RF) (ppbv/area count x 10^{-5})
1	Freon 12	3.65	3.465	13.89
2	Methyl chloride	4.30	0.693	
3	Freon 114	5.13	0.578	22.32
4	Vinyl chloride	5.28	0.406	
5	Methyl bromide	6.44		26.34
6	Ethyl chloride	7.06	0.413	
7	Freon 11	8.60	6.367	1.367
8	Vinylidene chloride	9.51	0.347	
9	Dichloromethane	9.84	0.903	
10	Trichlorotrifluoroethane	10.22	0.374	3.955
11	1,1-Dichloroethane	11.10	0.359	
12	cis-1,2-Dichloroethylene	11.99	0.368	
13	Chloroform	12.30	1.059	11.14
14	1,2-Dichloroethane	12.92	0.409	
15	Methyl chloroform	13.12	0.325	3.258
16	Benzene	13.51	0.117	
17	Carbon tetrachloride	13.64	1.451	1.077
18	1,2-Dichloropropane	14.26	0.214	
19	Trichloroethylene	14.50	0.327	8.910
20	cis-1,3-Dichloropropene	15.31		
21	trans-1,3-Dichloropropene	15.83		
22	1,1,2-Trichloroethane	15.93	0.336	
23	Toluene	16.17	0.092	
24	1,2-Dibromoethane (EDB)	16.78	0.366	5.137
25	Tetrachloroethylene	17.31	0.324	1.449
26	Chlorobenzene	18.03	0.120	
27	Ethylbenzene	18.51	0.092	
28	m,p-Xylene	18.72	0.095	
29	Styrene	19.12	0.143	
30	1,1,2,2-Tetrachloroethane	19.20		9.856
31	o-Xylene	19.23		
32	4-Ethyltoluene	20.82	0.100	
33	1,3,5-Trimethylbenzene	20.94	0.109	
34	1,2,4-Trimethylbenzene	21.46	0.111	
35	m-Dichlorobenzene	21.50		
36	Benzyl chloride	21.56		
37	p-Dichlorobenzene	21.67	0.188	
38	o-Dichlorobenzene	22.12	0.188	
39	1,2,4-Trichlorobenzene	24.88	0.667	
40	Hexachlorobutadiene	25.82	0.305	1.055

[1] Refer to Figures 15 and 16 for peak location

TABLE 8. TYPICAL RETENTION TIME (minutes) FOR SELECTED ORGANICS USING GC-FID-ECD-PID* ANALYTICAL SYSTEM

Compound	Retention Time (minutes)		
	FID	ECD	PID
Acetylene	2.984	—	—
1,3-Butadiene	3.599	—	3.594
Vinyl chloride	3.790	—	3.781
Chloromethane	5.137	—	—
Chloroethane	5.738	—	—
Bromoethane	8.154	—	—
Methylene Chloride	9.232	—	9.218
trans-1,2-Dichloroethylene	10.077	—	10.065
1,1-Dichloroethane	11.190	—	—
Chloroprene	11.502	—	11.491
Perfluorobenzene	13.077	13.078	13.069
Bromochloromethane	13.397	13.396	13.403
Chloroform	13.768	13.767	13.771
1,1,1-Trichloroethane	14.151	14.153	14.158
Carbon Tetrachloride	14.642	14.667	14.686
Benzene/1,2-Dichloroethane	15.128	—	15.114
Perfluorotoluene	15.420	15.425	15.412
Trichloroethylene	17.022	17.024	17.014
1,2-Dichloropropene	17.491	17.805	17.522
Bromodichloromethane	18.369	—	—
trans-1,3-Dichloropropylene	19.694	19.693	19.688
Toluene	20.658	—	20.653
cis-1,3-Dichloropropylene	21.461	21.357	21.357
1,1,2-Trichloroethane	21.823	—	—
Tetrachloroethylene	22.340	22.346	22.335
Dibromochloromethane	22.955	22.959	22.952
Chlorobenzene	24.866	—	24.861
m/p-Xylene	25.763	—	25.757
Styrene/o-Xylene	27.036	—	27.030
Bromofluorobenzene	28.665	28.663	28.660
1,1,2,2-Tetrachloroethane	29.225	29.227	29.228
m-Dichlorobenzene	32.347	32.345	32.342
p-Dichlorobenzene	32.671	32.669	32.666
o-Dichlorobenzene	33.885	33.883	33.880

* Varian® 3700 GC equipped with J & W Megabore® DB 624 Capillary Column (30 m X 0.53 I.D. mm) using helium carrier gas.

TABLE 9. GC-MS-SIM CALIBRATION TABLE

Last Update: 18 Jan. 86 7:54 am
Reference Peak Window: 5:00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 **Uncalibrated Peak RF:** 0.00 **Multiplier:** 1.000

Ret. Time	Pk#	Signal	Descr	Amt pptv	Lvl	[Area]	Pk-type	Partial Name
5.008	1	Mass	85.00 amu	13620	1	72974	1	FREON 12
5.690	2	Mass	50.00 amu	12720	1	36447	1	METHYLCHLORIDE
6.552	3	Mass	85.00 amu	8380	1	81251	1	FREON 114
6.709	4	Mass	62.00 amu	8050	1	20118	1	VINYLCHLORIDE
7.831	5	Mass	94.00 amu	12210	1	28265	1	METHYLBROMIDE
8.431	6	Mass	64.00 amu	12574	1	16149	1	ETHYLCHLORIDE
9.970	7	Mass	101.00 amu	12380	1	80088	1	FREON 11
10.929	8	Mass	61.00 amu	7890	1	38954	1	VINDENECHLORI
11.209	9	Mass	49.00 amu	12760	1	43307	1	DICHLOROMETHA
11.331	10	Mass	41.00 amu	12650	1	1945	1	ALLYLCHLORIDE
11.595	11	Mass	151.00 amu	7420	1	40530	1	3CHL3FLUETHAN
12.502	12	Mass	63.00 amu	12710	1	61595	1	1,1DICHLOETHA
13.403	13	Mass	61.00 amu	12630	1	50900	1	c-1,2DICHLETH
13.747	14	Mass	83.00 amu	7670	1	40585	1	CHLOROFORM
14.387	15	Mass	62.00 amu	9040	1	33336	1	1,2DICHLETHAN
14.623	16	Mass	97.00 amu	8100	1	38503	1	METHCHLOROFORM
15.038	17	Mass	78.00 amu	10760	1	69119	1	BENZENE
15.183	18	Mass	117.00 amu	8340	1	42737	1	CARBONTETRACH
15.829	19	Mass	63.00 amu	12780	1	38875	1	1,2DICHLPROPA
16.096	20	Mass	130.00 amu	8750	1	30331	1	TRICHLETHENE
16.956	21	Mass	75.00 amu	4540	1	17078	1	c-1,3DICHLPRO
17.492	22	Mass	75.00 amu	3380	1	13294	1	t-1,3DICHLPRO
17.610	23	Mass	97.00 amu	12690	1	32480	1	1,1,2CHLETHAN
17.862	24	Mass	91.00 amu	10010	1	88036	1	TOLUENE
18.485	25	Mass	107.00 amu	6710	1	33330	1	EDB
19.012	26	Mass	166.00 amu	7830	1	43454	1	TETRACHLETHEN
19.729	27	Mass	112.00 amu	7160	1	44224	1	CHLOROBENZENE
20.195	28	Mass	91.00 amu	12740	1	127767	1	ETHYLBENZENE
20.407	29	Mass	91.00 amu	25400	1	200973	1	m,p-XYLENE
20.806	30	Mass	104.00 amu	12390	1	38332	1	STYRENE
20.916	31	Mass	83.00 amu	11690	1	64162	1	TETRACHLETHAN
20.921	32	Mass	91.00 amu	11085	1	90096	1	o-XYLENE
22.528	33	Mass	105.00 amu	12560	1	108747	1	4-ETHYLTOLUEN
22.648	34	Mass	105.00 amu	12620	1	83666	1	1,3,5METHBENZ
23.179	35	Mass	105.00 amu	12710	1	70833	1	1,2,4METHBENZ
23.307	36	Mass	146.00 amu	12650	1	57409	1	m-DICHLBENZEN
23.317	37	Mass	91.00 amu	7900	1	50774	1	BENZYLCHLORID
23.413	38	Mass	146.00 amu	12390	1	58127	1	p-DICHLBENZEN
23.885	39	Mass	146.00 amu	13510	1	52233	1	o-DICHLBENZEN
26.714	40	Mass	180.00 amu	15520	1	18967	1	1,2,4CHLBENZE
27.680	41	Mass	225.00 amu	7470	1	43920	1	HEXACHLBUTADI

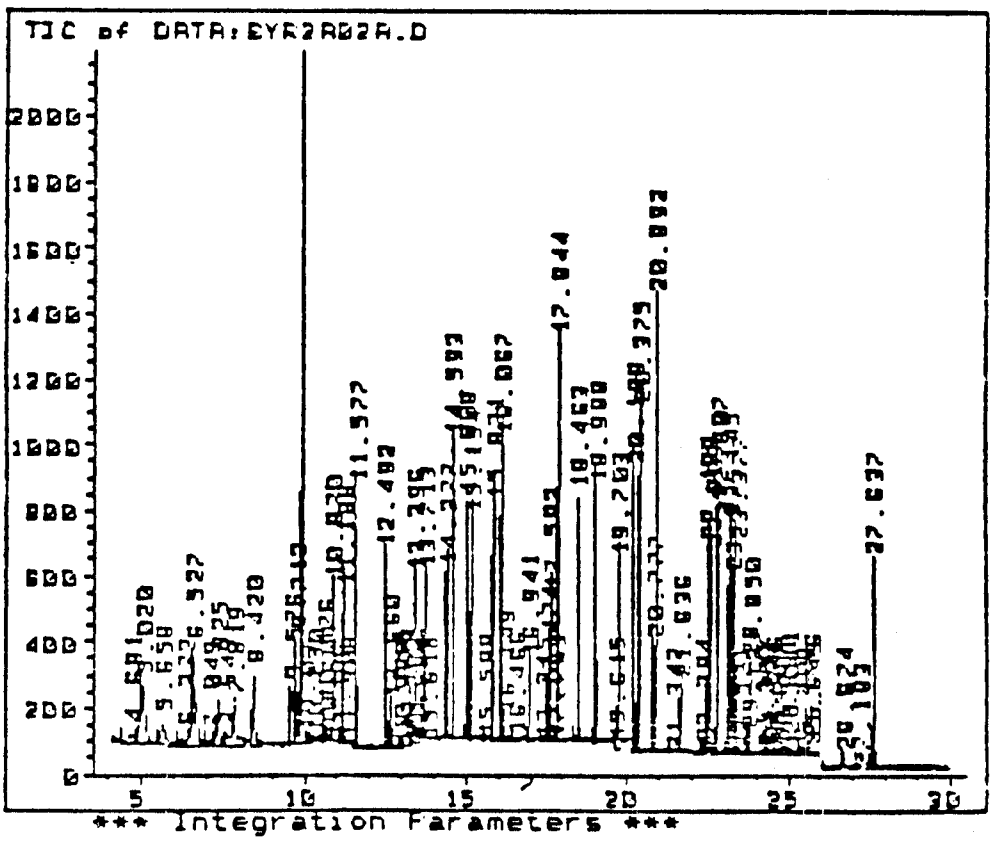
TABLE 10. EXAMPLE OF HARD-COPY OF GC-MS-SIM ANALYSIS

```
Data file: DATA:SYR2A02A.D
File type: GC / MS DATA FILE

Name Info: SYR 1
Misc Info:
Operator : JDF

Date     :  8 Jan 87  10:02 am
Instrment: MS_5970
Inlet    : GC

Sequence index :     1
Als bottle num :     2
Replicate num  :     1
```



*** Integration Parameters ***

```
FALSE : Shoulder Detection Enabled
0.020 : Expected Peak Width (Min)
   11 : Initial Peak Detection Threshold

4.000   THRESHOLD      5.000
4.000   PEAK_WIDTH     0.200
9.800   PEAK_WIDTH     0.060
```

TABLE 10. EXAMPLE OF HARD-COPY OF GC-MS-SIM ANALYSIS (cont.)

Operator: JDP **8 Jan 87 10:02 am**
Sample Info: SRY 1
Misc Info:
Integration File Name: DATA:SYR2A02A.I

Sequence Index: 1 **Bottle Number 2:**

Last Update: 8 Jan. 86 8:13 am
Reference Peak Window: 5:00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 Uncalibrated Peak RF: 0.00 Multiplier: 1.667

Peak Num.	Int Type	Ret Time	Signal Description	Compound Name	Area	Amount	
1	1 PP	5.020	Mass 85.00 amu	FREON 12	12893	4011	pptv
2	1 PP	5.654	Mass 50.00 amu	METHYLCHLORIDE	4445	2586	pptv
3	1 BP	6.525	Mass 85.00 amu	FREON 114	7067	1215	pptv
4	1 PB	6.650	Mass 62.00 amu	VINYLCHLORIDE	2892	1929	pptv
5	1 BP	7.818	Mass 94.00 amu	METHYLBROMIDE	2401	1729	pptv
6	1 BB	8.421	Mass 64.00 amu	ETHYLCHLORIDE	2134	2769	pptv
7	1 BV	9.940	Mass 101.00 amu	FREON 11	25069	6460	pptv
8	1 BP	10.869	Mass 61.00 amu	VINDENECHLOR	5034	1700	pptv
9	1 BP	11.187	Mass 49.00 amu	DICHLOROMETH	4803	2348	pptv
10	1 PP	11.223	Mass 41.00 amu	ALLYLCHLORID	761	8247	pptv
11	1 BP	11.578	Mass 151.00 amu	3CHL3FLUETHA	5477	1672	pptv
12	1 BP	12.492	Mass 63.00 amu	1,1DICHLOETH	5052	1728	pptv
13	1 VP	13.394	Mass 61.00 amu	c-1,2DICHLET	4761	1970	pptv
14	1 PH	13.713	Mass 83.00 amu	CHLOROFORM	5327	1678	pptv
15	1 BP	14.378	Mass 62.00 amu	1,2DICHLETHA	5009	2263	pptv
16	1 PB	14.594	Mass 97.00 amu	METHCHLOROFO	6656	2334	pptv
17	1 VP	15.009	Mass 78.00 amu	BENZENE	8332	2167	pptv
18	1 VP	15.154	Mass 117.00 amu	CARBONTETRAC	5888	1915	pptv
19	1 BB	15.821	Mass 63.00 amu	1,2DICHLPROP	3283	1799	pptv
20	1 BB	16.067	Mass 130.00 amu	TRICHLETHENE	4386	2109	pptv
21	1 PB	16.941	Mass 75.00 amu	c-1,3DICHLPR	2228	987.3	pptv
22	1 BP	17.475	Mass 75.00 amu	t-1,3DICHLPR	1626	689.2	pptv
23	1 BB	17.594	Mass 97.00 amu	1,1,2CHLRTHA	2721	1772	pptv
24	1 BV	17.844	Mass 91.00 amu	TOLUENE	14417	2733	pptv
25	1 PB	18.463	Mass 107.00 amu	EDB	4070	1365	pptv
26	1 PH	18.989	Mass 166.00 amu	TETRACHLETHE	6874	2065	pptv
27	1 PB	19.705	Mass 112.00 amu	CHLOROBENZEN	5648	1524	pptv
28	1 BP	20.168	Mass 91.00 amu	ETHYLBENZENE	11084	1842	pptv
29	1 PB	20.372	Mass 91.00 amu	m,p-XYLENE	17989	37909	pptv
30	1 BV	20.778	Mass 104.00 amu	STYRENE	3145	1695	pptv
31	1 BH	20.887	Mass 83.00 amu	TETRACHLETHA	4531	1376	pptv
32	1 BP	20.892	Mass 91.00 amu	o-XYLENE	9798	2010	pptv
33	1 VV	22.488	Mass 105.00 amu	4-ETHYLTOLUE	7694	14811	pptv
34	1 VB	22.609	Mass 105.00 amu	1,3,5METHBEN	6781	1705	pptv
35	1 BB	23.114	Mass 105.00 amu	1,2,4METHBEN	7892	2095	pptv
36	1 BV	23.273	Mass 146.00 amu	m-DICHLBENZE	3046	1119	pptv
37	1 VV	23.279	Mass 91.00 amu	BENZYLCHLORI	3880	1006	pptv
38	1 VB	23.378	Mass 146.00 amu	p-DICHLBENZE	6090	2164	pptv
39	1 BP	23.850	Mass 146.00 amu	o-DICHLBENZE	2896	1249	pptv
40	1 BB	26.673	Mass 180.00 amu	1,2,4CHLBENZ	562	767.1	pptv
41	1 BB	27.637	Mass 225.00 amu	HEXACHLBUTAD	6309	1789	pptv

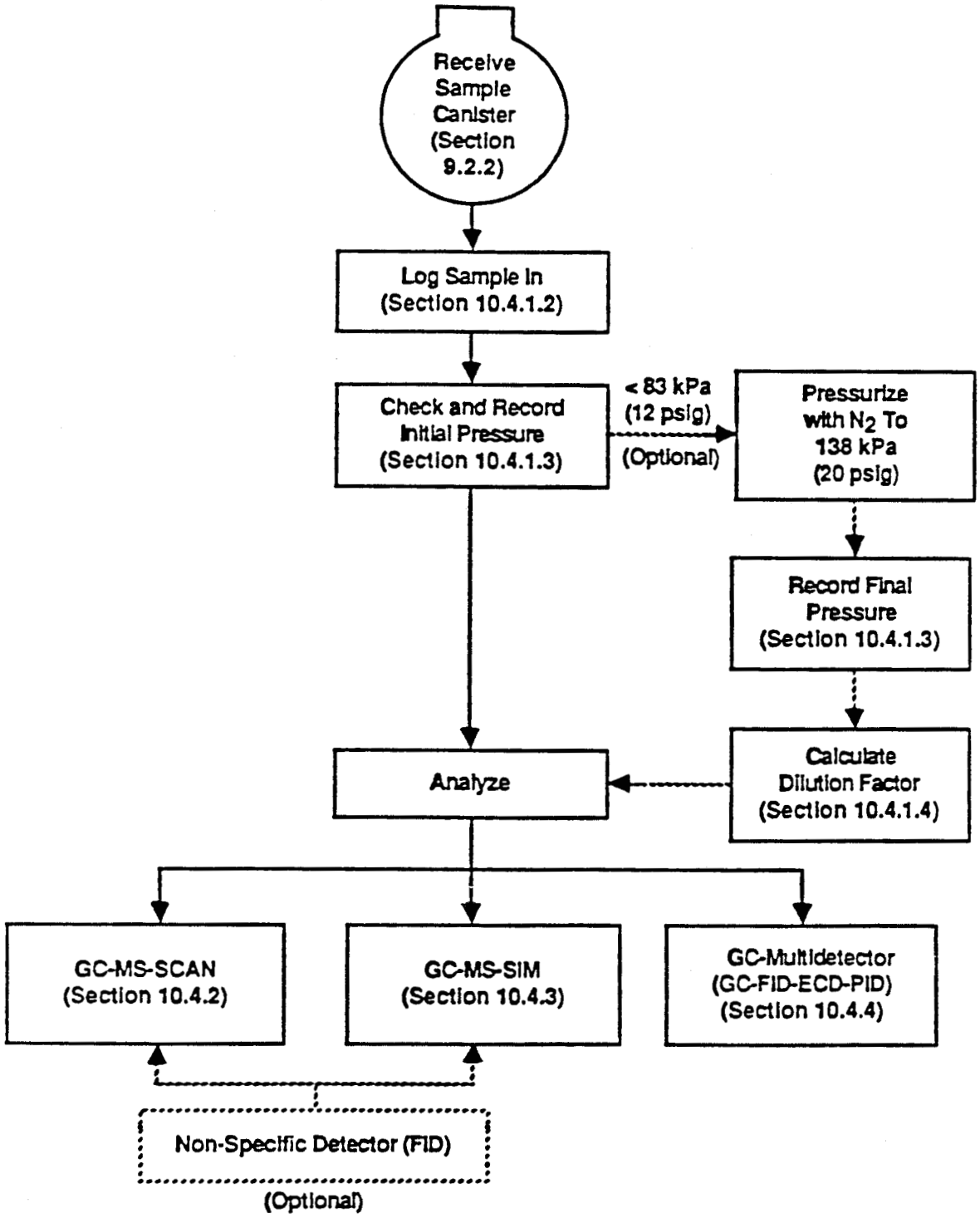

Receive Sample Canister (Section 9.2.2)
Log Sample In (Section 10.4.1.2)
Check and Record Initial Pressure (Section 10.4.1.3)
< 83 kPa (12 psig)
(Optional)
Pressurize with N_2 To 138 kPa (20 psig)
Record Final Pressure (Section 10.4.1.3)
Calculate Dilution Factor (Section 10.4.1.4)
Analyze
GC-MS-SCAN (Section 10.4.2)
GC-MS-SIM (Section 10.4.3)
GC-Multidetector (GC-FID-ECD-PID) (Section 10.4.4)
Non-Specific Detector (FID)
(Optional)

FIGURE 1. ANALYTICAL SYSTEMS AVAILABLE FOR CANISTER VOC IDENTIFICATION AND QUANTITATION

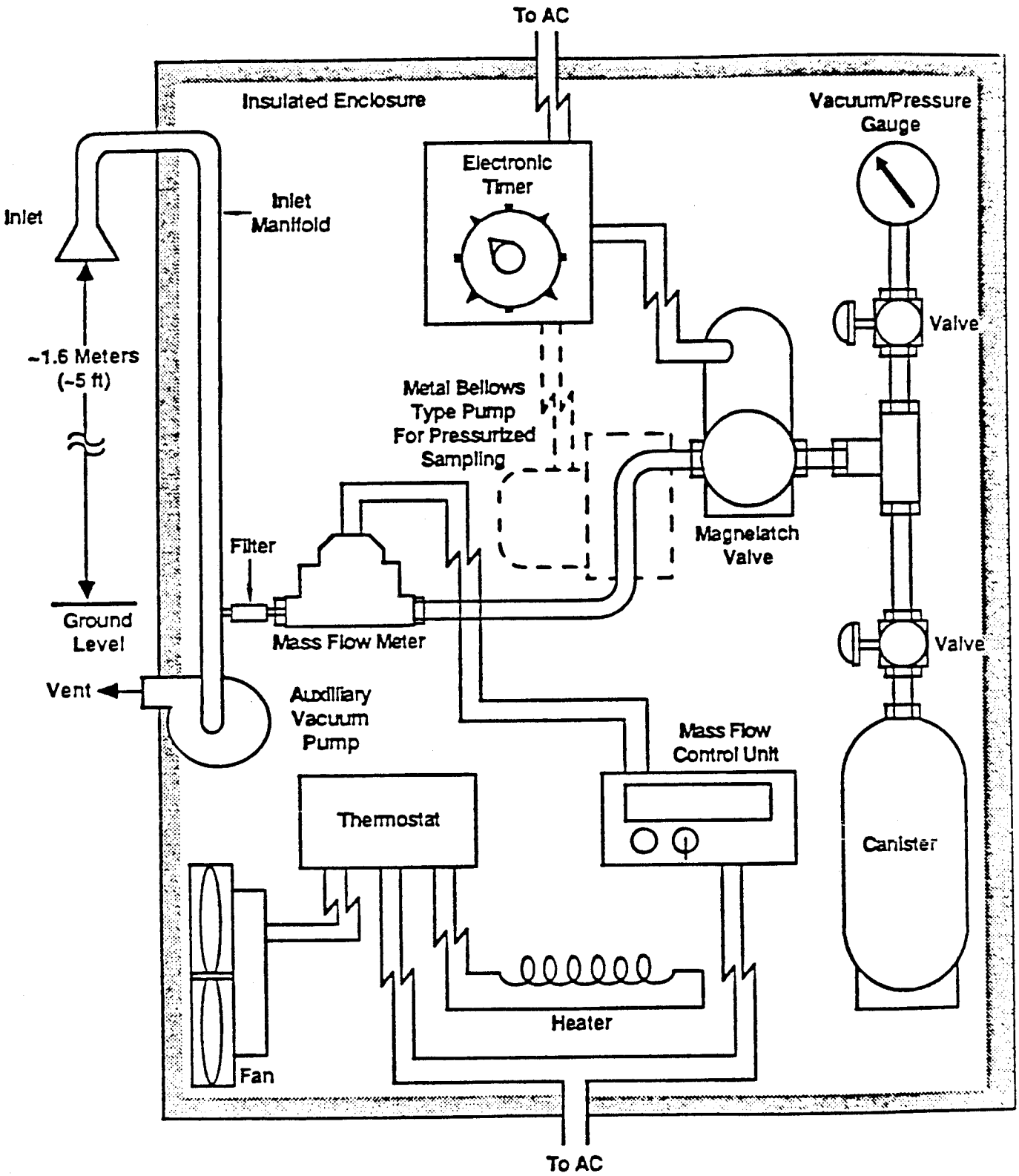


FIGURE 2. SAMPLER CONFIGURATION FOR SUBATMOSPHERIC PRESSURE OR PRESSURIZED CANISTER SAMPLING

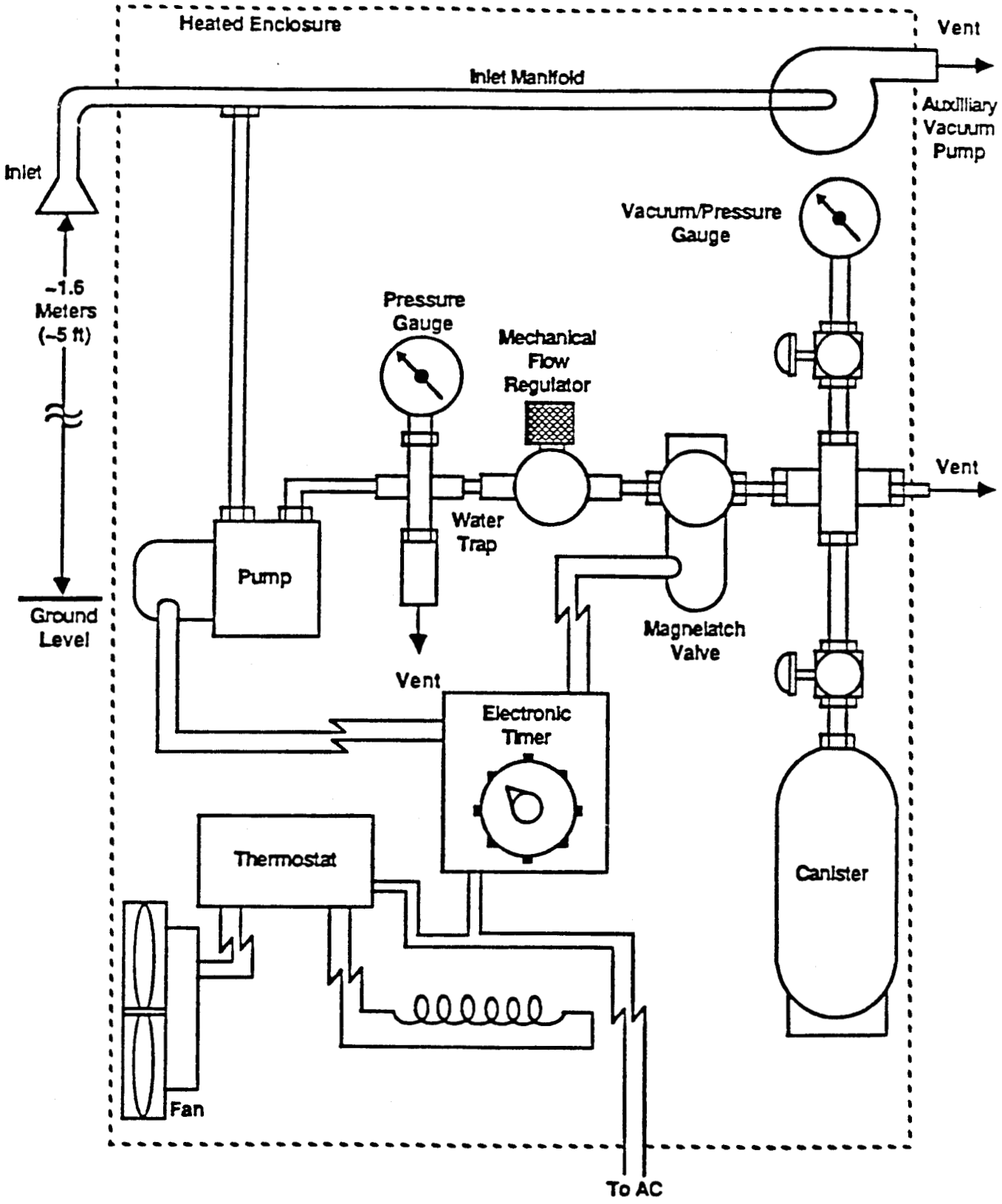


FIGURE 3. ALTERNATIVE SAMPLER CONFIGURATION FOR PRESSURIZED CANISTER SAMPLING

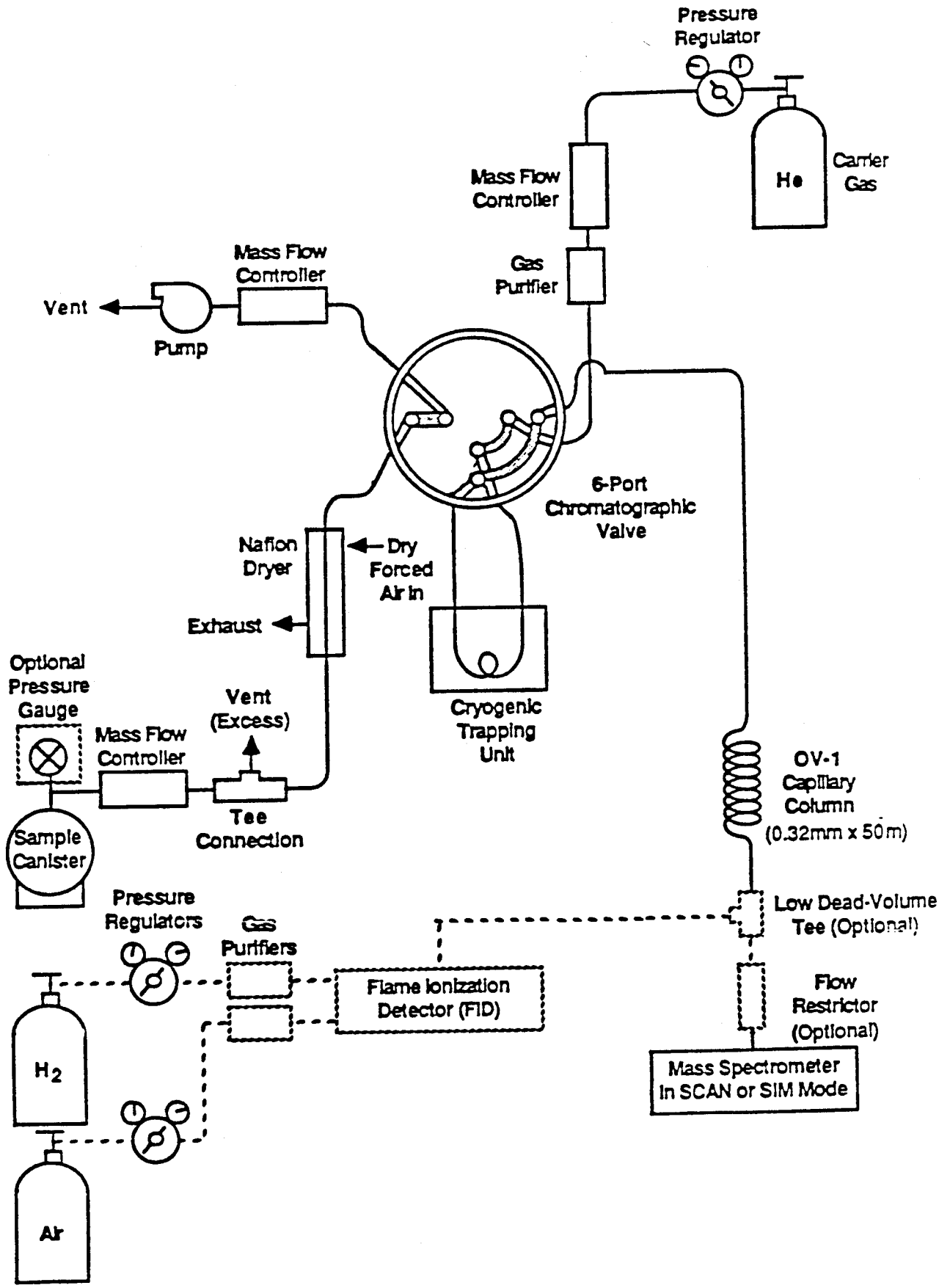


FIGURE 4. CANISTER ANALYSIS UTILIZING GC-MS-SCAN-SIM ANALYTICAL SYSTEM WITH OPTIONAL FLAME IONIZATION DETECTOR WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

U.S. EPA Compendium Method T014 (1988)

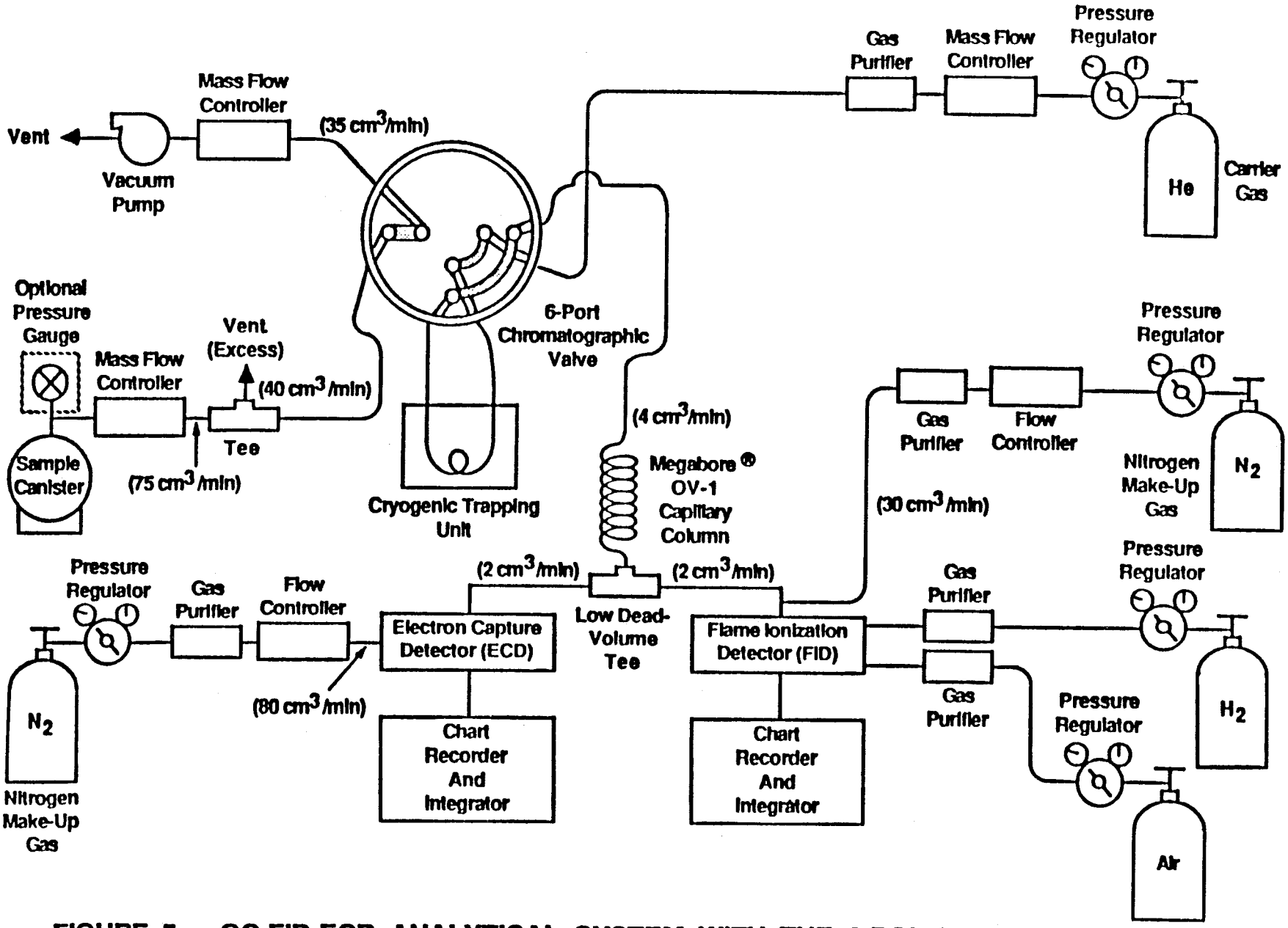


FIGURE 5. GC-FID-ECD ANALYTICAL SYSTEM WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

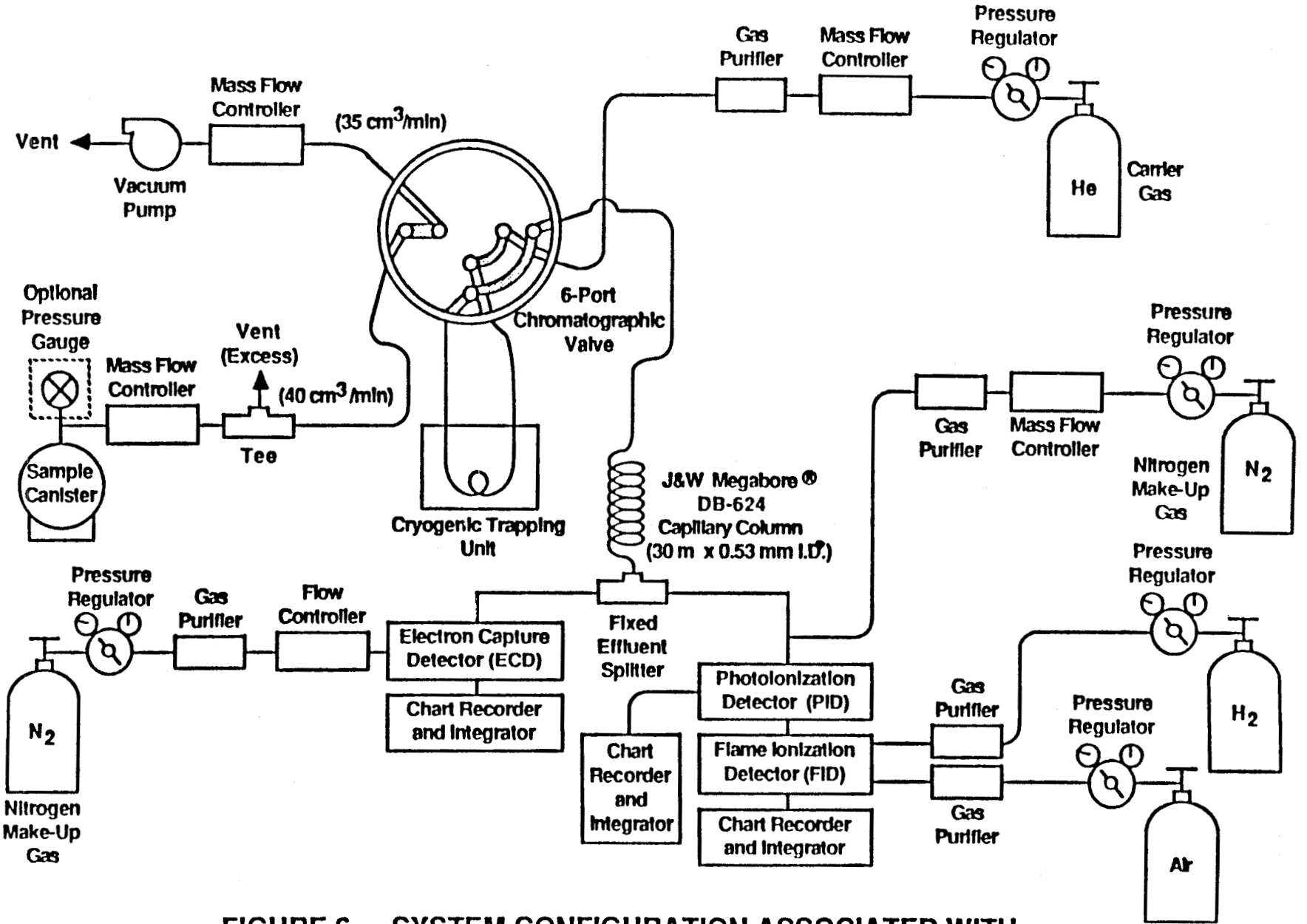


FIGURE 6. SYSTEM CONFIGURATION ASSOCIATED WITH THE GC-FID-ECD-PID ANALYTICAL SYSTEM WITH THE 6-PORT CHROMATOGRAPHIC VALVE IN THE SAMPLE DESORPTION MODE

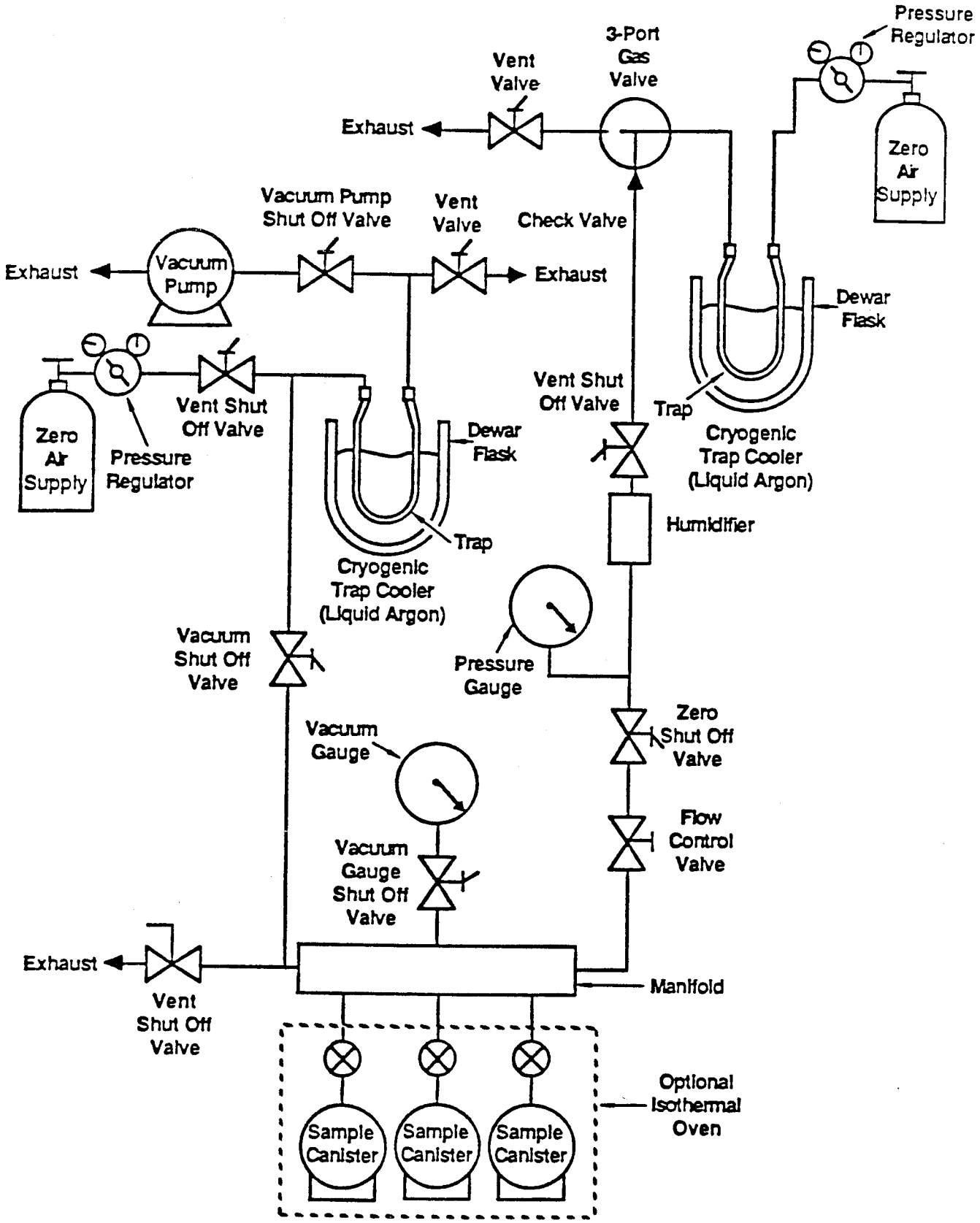


FIGURE 7. CANISTER CLEANING SYSTEM

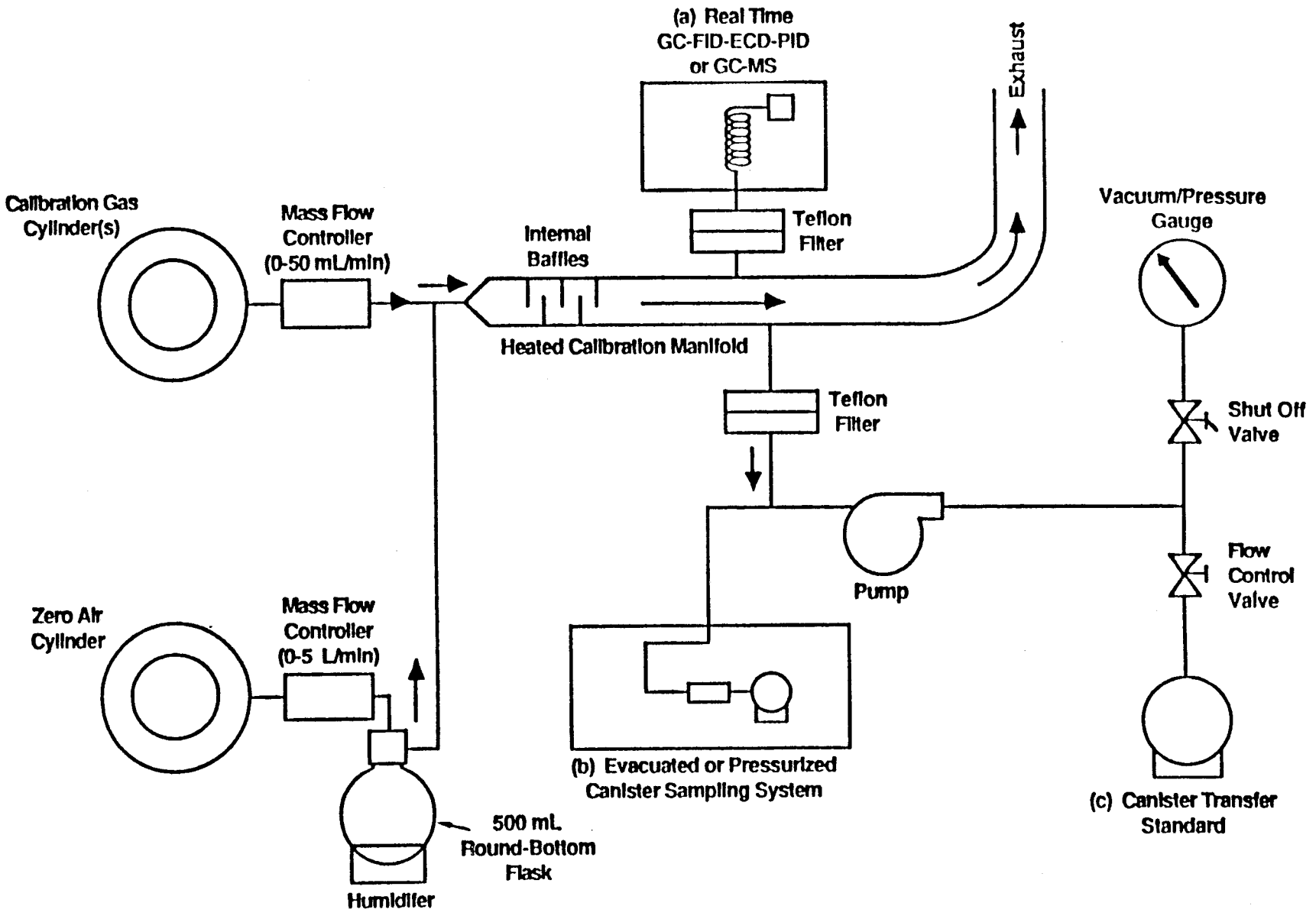
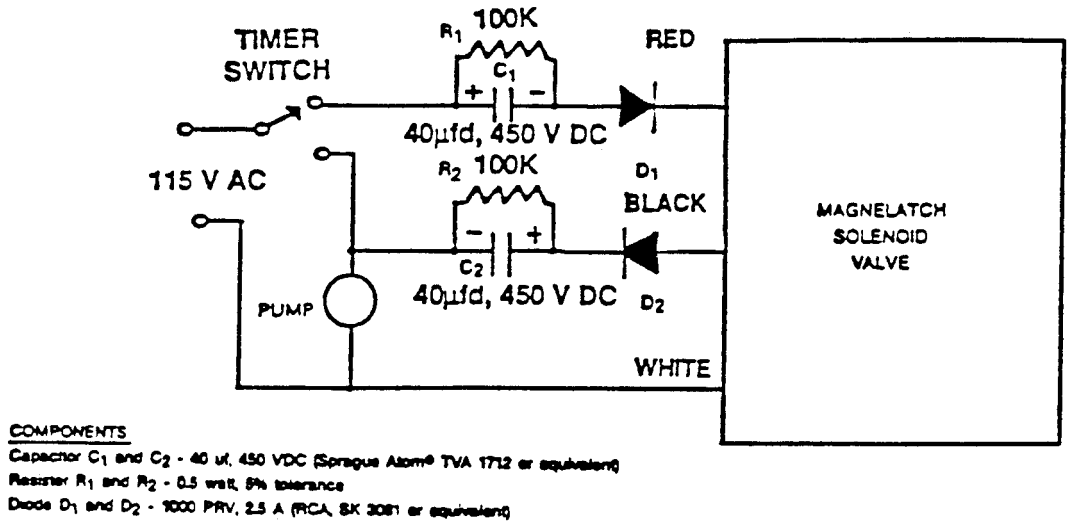


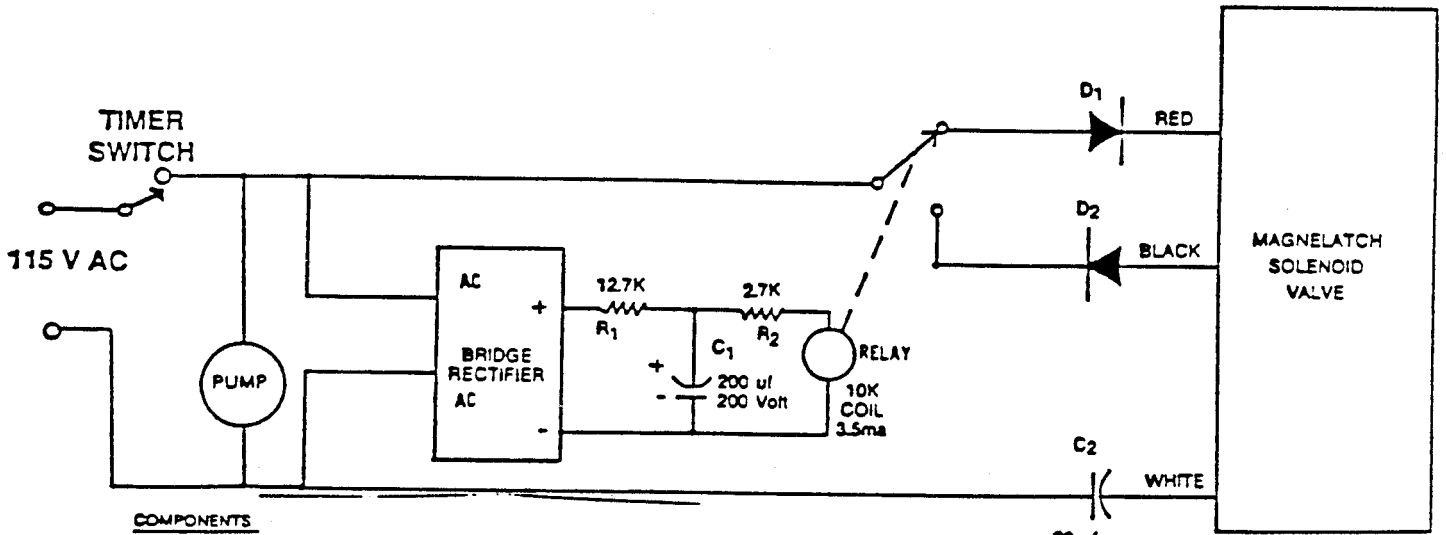
FIGURE 8. SCHEMATIC OF CALIBRATION SYSTEM AND MANIFOLD FOR (a) ANALYTICAL SYSTEM CALIBRATION, (b) TESTING CANISTER SAMPLING SYSTEM AND (c) PREPARING CANISTER TRANSFER STANDARDS.



COMPONENTS

Capacitor C_1 and C_2 - 40 uf, 450 VDC (Sprague Atom® TVA 1712 or equivalent)
Resistor R_1 and R_2 - 0.5 watt, 5% tolerance
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit For Operating Magnelatch Valve



COMPONENTS

Bridge Rectifier - 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor C_1 - 200 uf, 250 VDC (Sprague Atom® TVA 1528 or equivalent)
Capacitor C_2 - 20 uf, 400 VDC Non-Polarized (Sprague Atom® TVAN 1652 or equivalent)
Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resistor R_1 and R_2 - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed To Handle Power Interruptions

FIGURE 9. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

CANISTER SAMPLING FIELD DATA SHEET

A. GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK
CHECK DATE: _____

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START			X	X
STOP				

PRESSURE

CANISTER PRESSURE	
X	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATE RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

ATTACH DATA SHEETS

FIGURE 10. CANISTER SAMPLING FIELD DATA SHEET

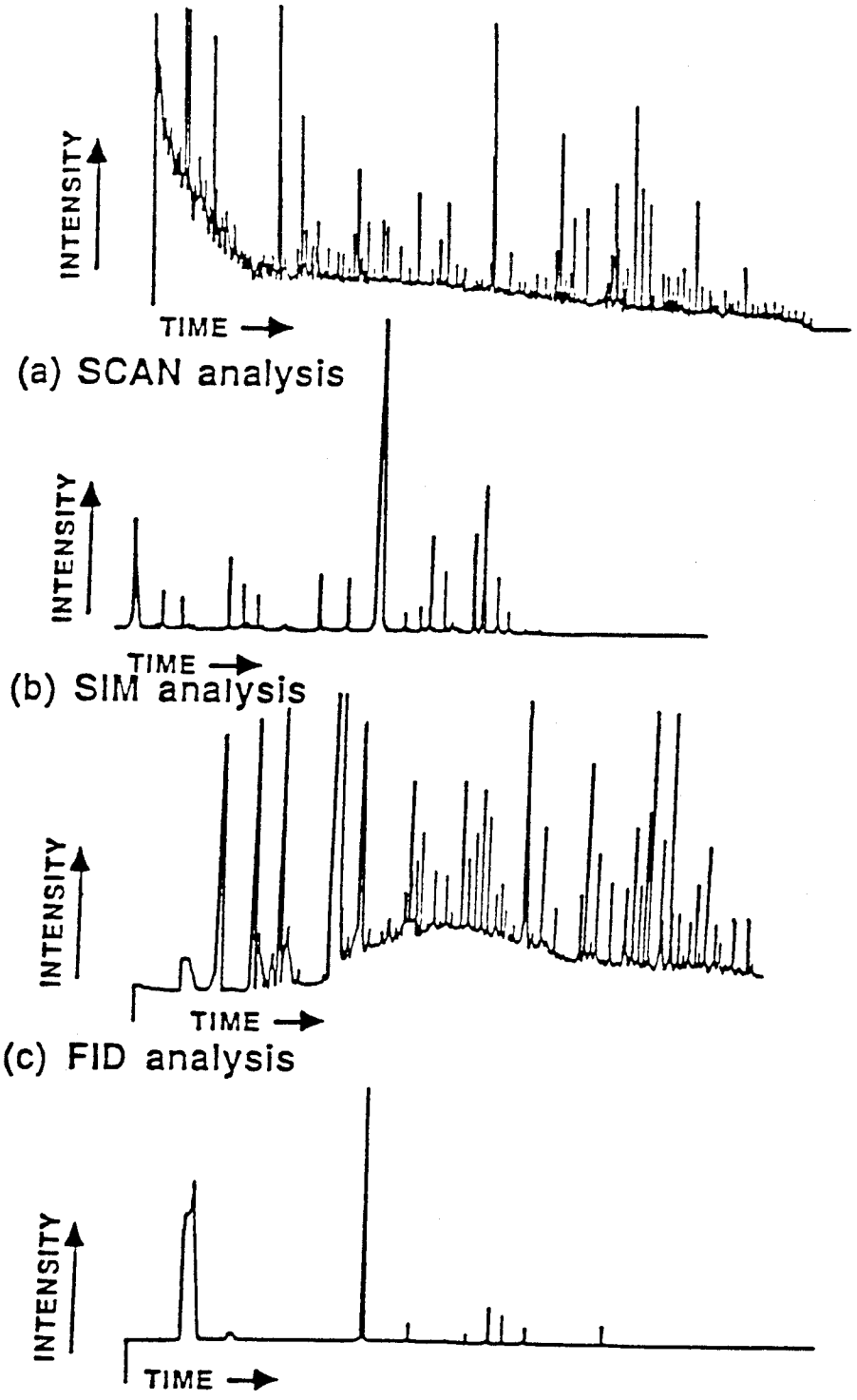


FIGURE 11. TYPICAL CHROMATOGRAMS OF A VOC SAMPLE ANALYZED BY GC-MS-SCAN-SIM MODE AND GC-MULTIDETECTOR MODE

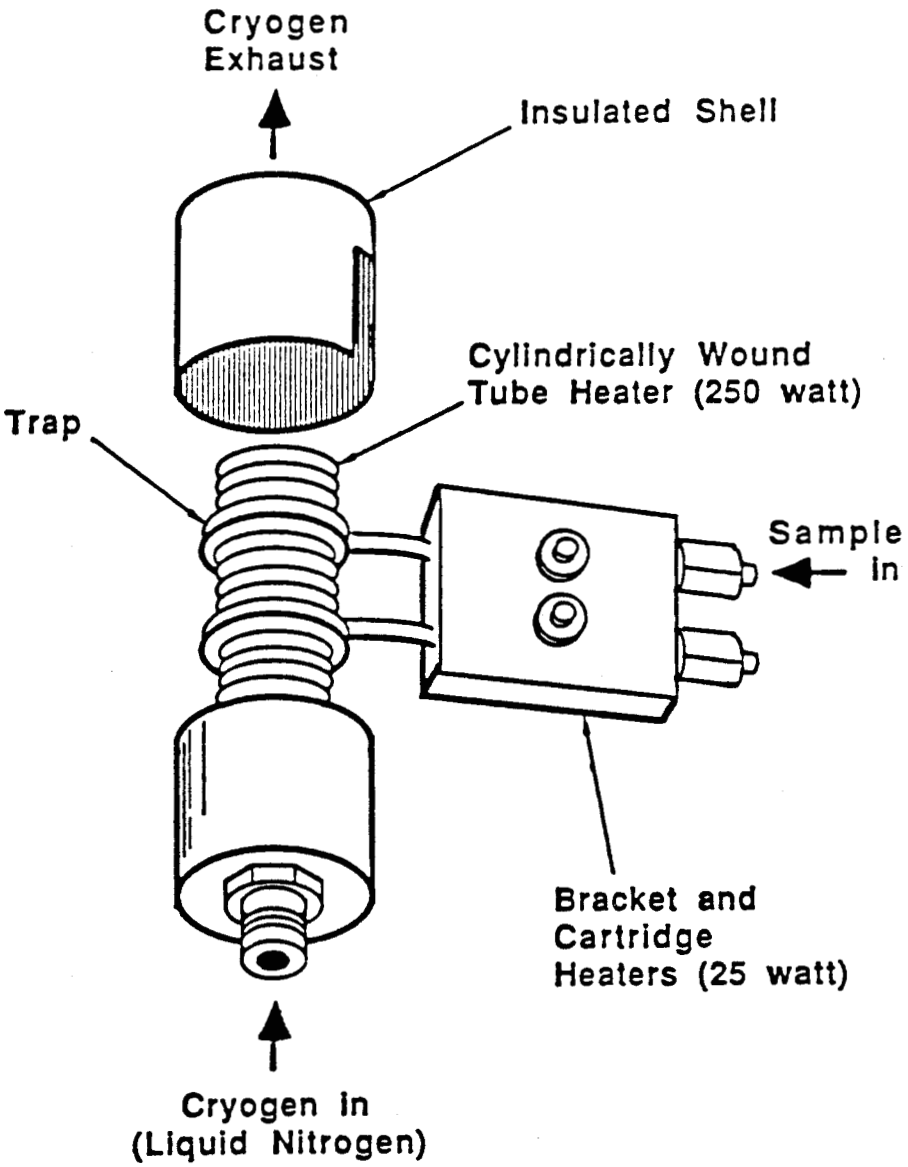


FIGURE 12. CRYOGENIC TRAPPING UNIT

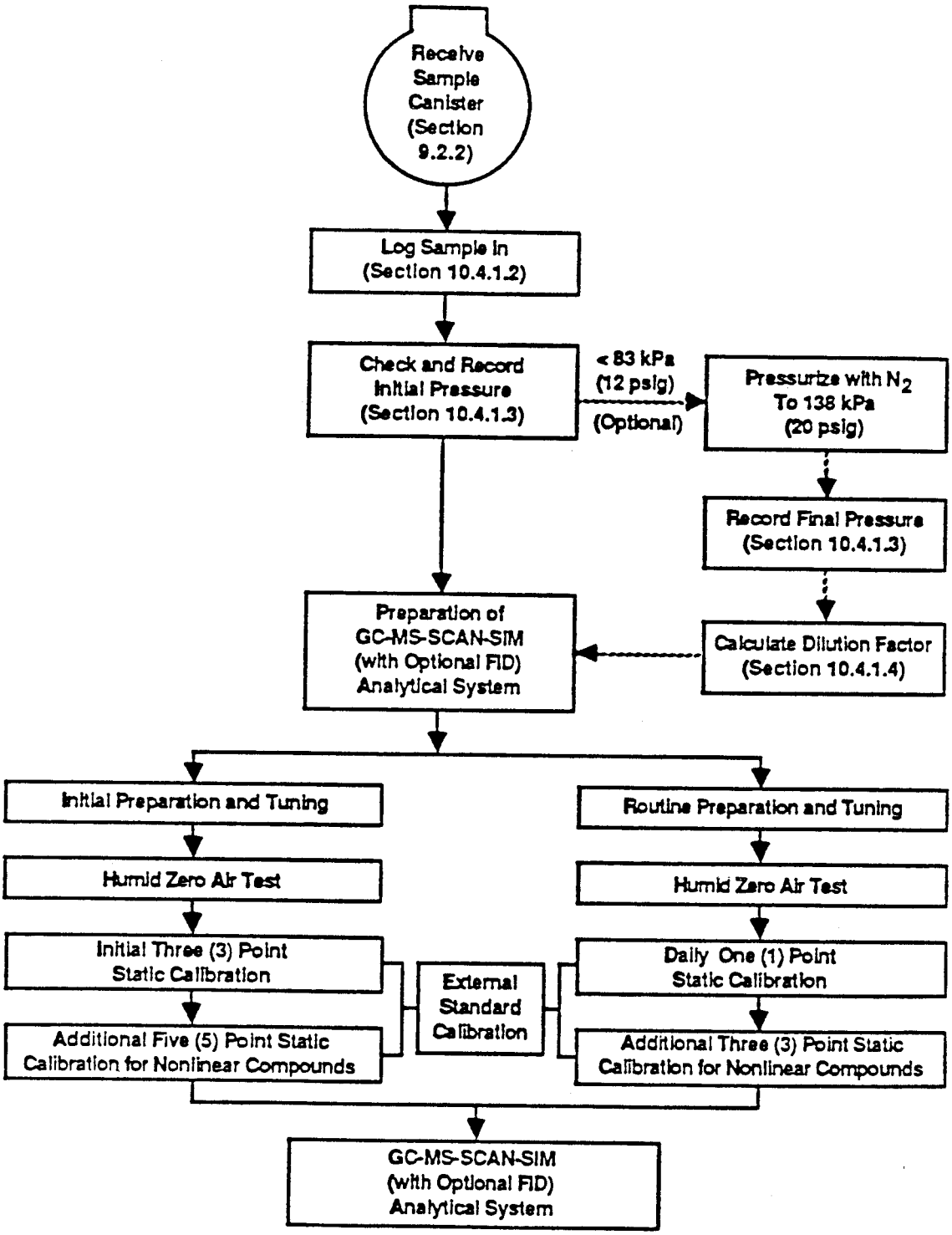

Receive Sample Canister (Section 9.2.2)
Log Sample In (Section 10.4.1.2)
Check and Record Initial Pressure (Section 10.4.1.3)
< 83 kPa (12 psig)
(Optional)
Pressurize with N_2 To 138 kPa (20 psig)
Record Final Pressure (Section 10.4.1.3)
Calculate Dilution Factor (Section 10.4.1.4)
Preparation of GC-MS-SCAN-SIM (with Optional FID) Analytical System
Initial Preparation and Tuning
Humid Zero Air Test
Initial Three (3) Point Static Calibration
Additional Five (5) Point Static Calibration for Nonlinear Compounds
Routine Preparation and Tuning
Humid Zero Air Test
Daily One (1) Point Static Calibration
Additional Three (3) Point Static Calibration for Nonlinear Compounds
External Standard Calibration
GC-MS-SCAN-SIM (with Optional FID) Analytical System

FIGURE 13. FLOWCHART OF GC-MS-SCAN-SIM ANALYTICAL SYSTEM PREPARATION (WITH OPTIONAL FID SYSTEM)

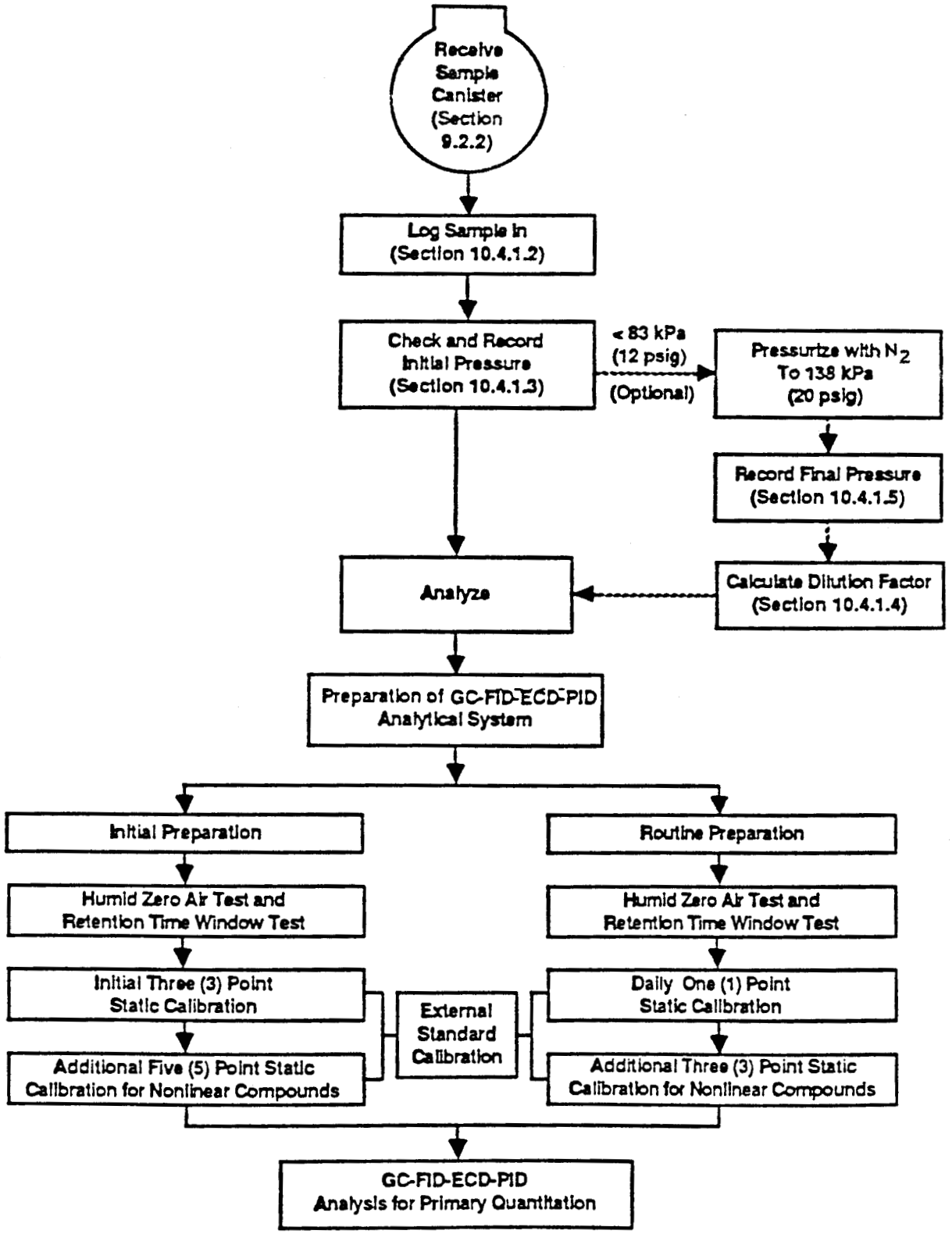

Receive Sample Canister (Section 9.2.2)
Log Sample In (Section 10.4.1.2)
Check and Record Initial Pressure (Section 10.4.1.3)
< 83 kPa (12 psig)
(Optional)
Pressurize with N_2 To 138 kPa (20 psig)
Record Final Pressure (Section 10.4.1.5)
Calculate Dilution Factor (Section 10.4.1.4)
Analyze
Preparation of GC-FID-ECD-PID Analytical System
Initial Preparation
Routine Preparation
Humid Zero Air Test and Retention Time Window Test
Humid Zero Air Test and Retention Time Window Test
Initial Three (3) Point Static Calibration
Additional Five (5) Point Static Calibration for Nonlinear Compounds
External Standard Calibration
Daily One (1) Point Static Calibration
Additional Three (3) Point Static Calibration for Nonlinear Compounds
GC-FID-ECD-PID Analysis for Primary Quantitation

FIGURE 14. FLOWCHART OF GC-FID-ECD-PID ANALYTICAL SYSTEM PREPARATION

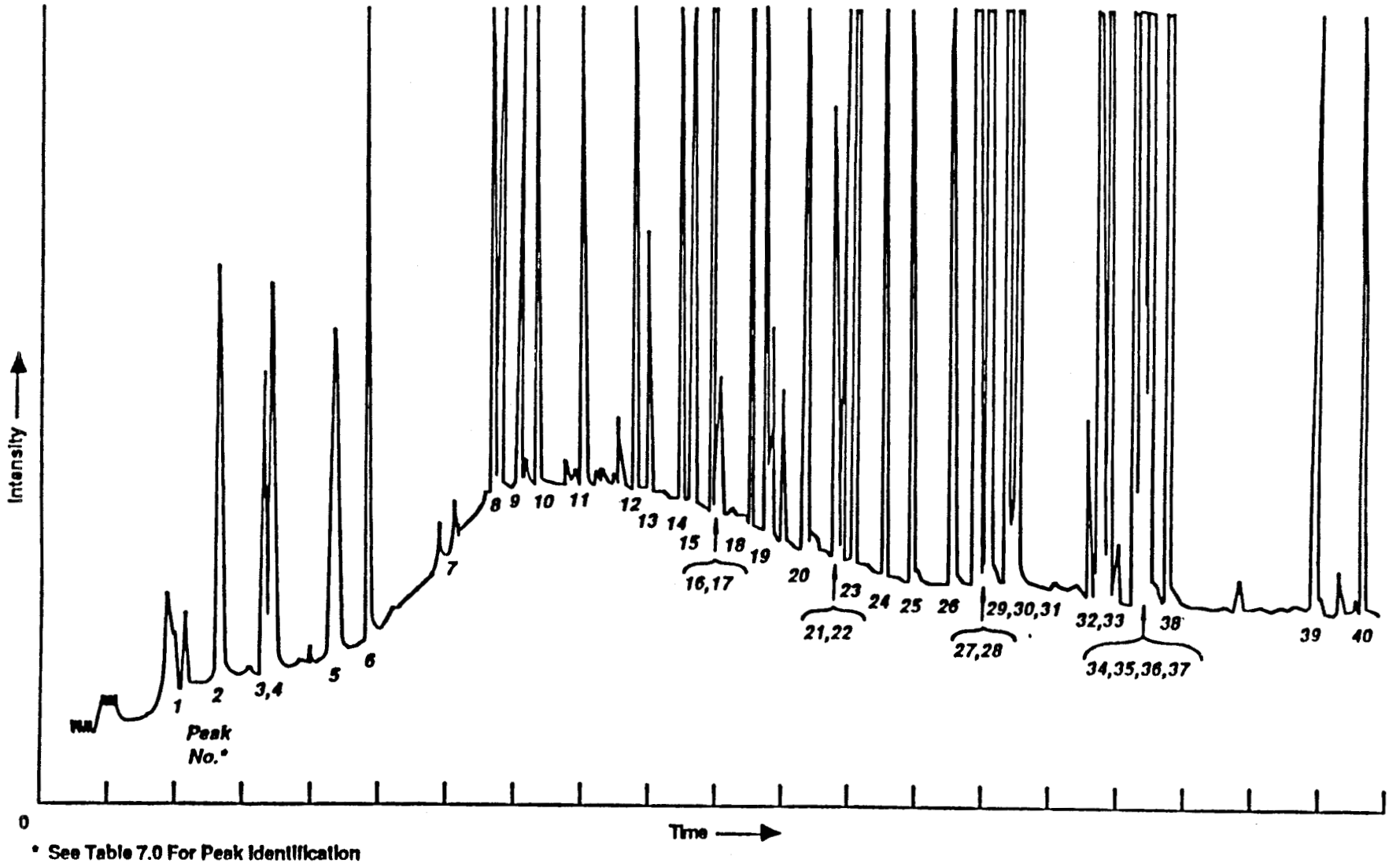
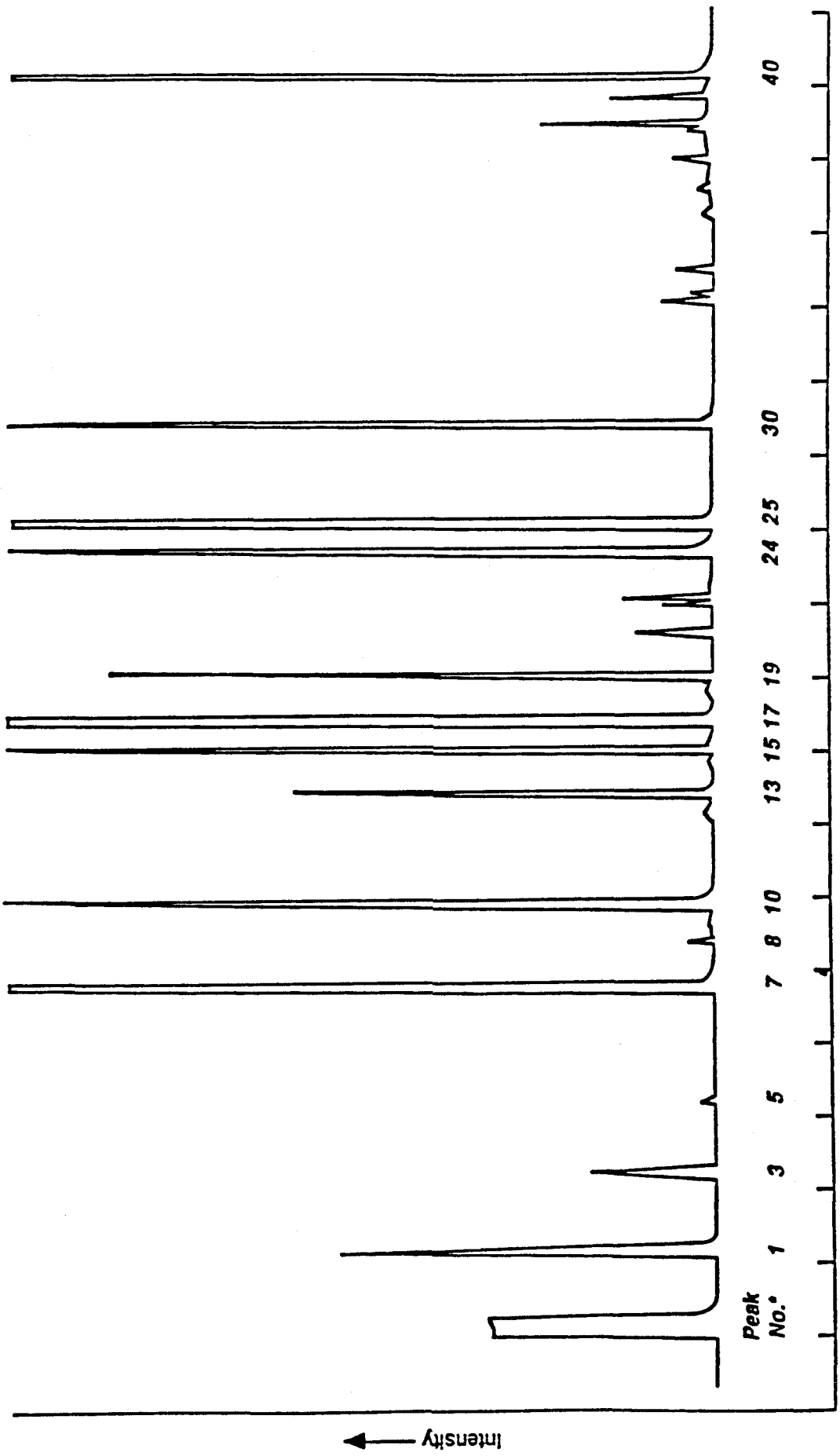
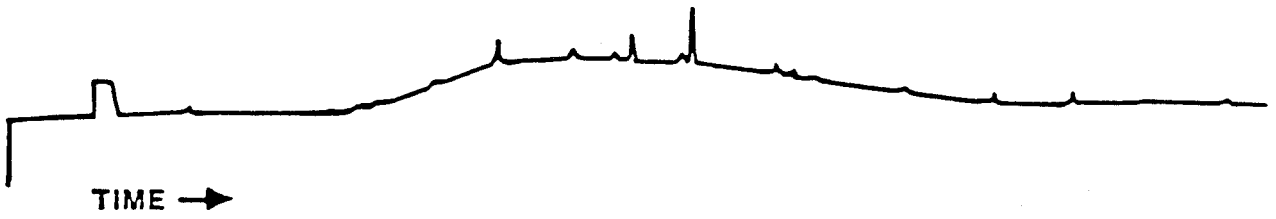


FIGURE 15. TYPICAL FID RESPONSE TO SELECTIVE VOCs

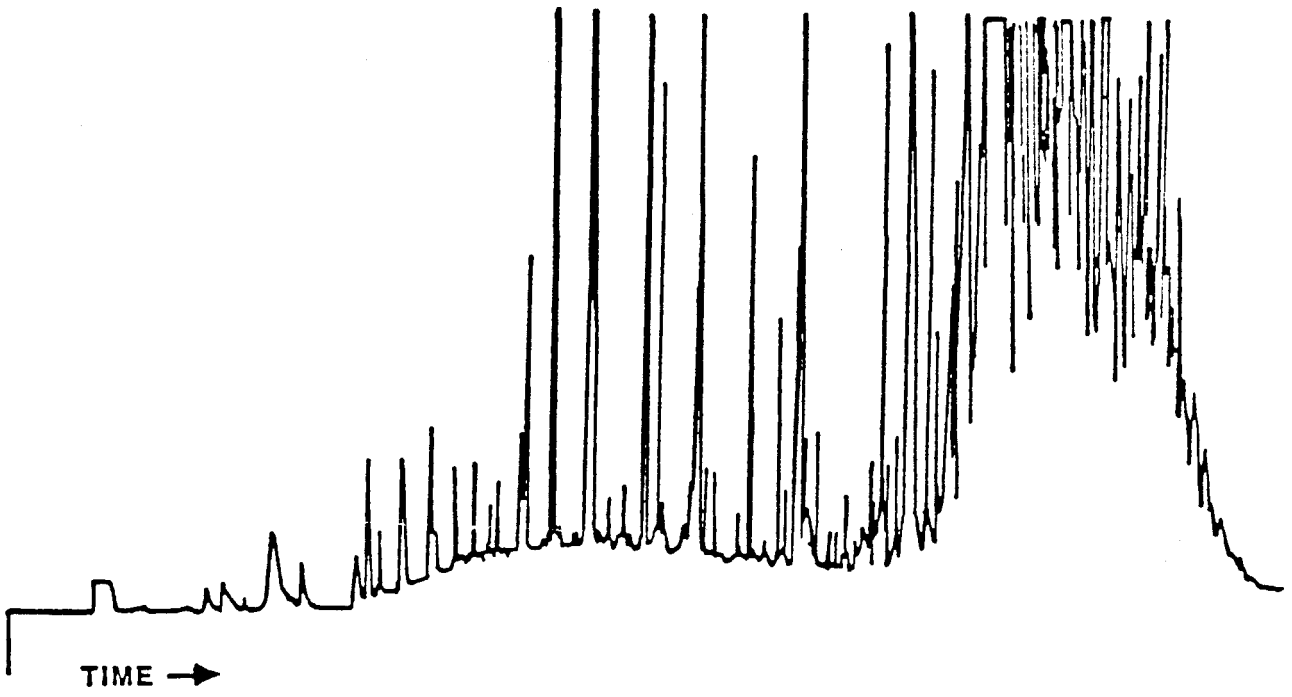


* See Table 7.0 For Peak Identification

FIGURE 16. TYPICAL ECD RESPONSE TO SELECTIVE VOCs



(a). Certified Sampler



(b). Contaminated Sampler

FIGURE 17. EXAMPLE OF HUMID ZERO AIR TEST RESULTS FOR A CLEAN SAMPLER (a) AND A CONTAMINATED SAMPLER (b)

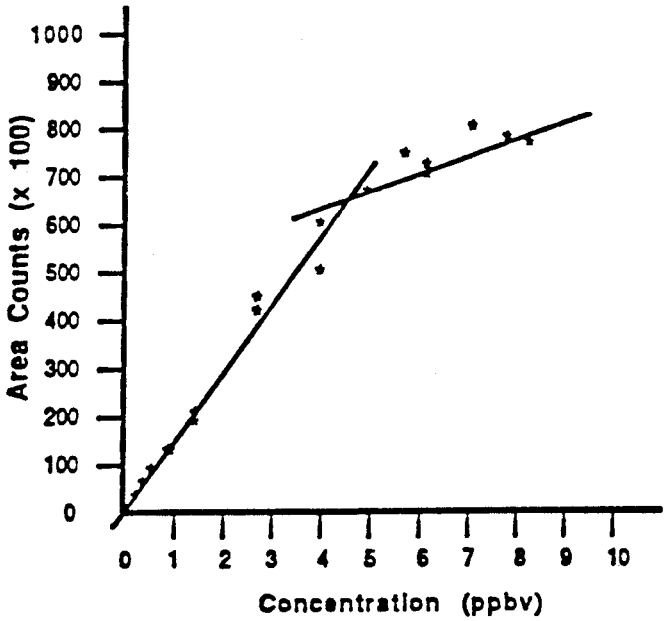


FIGURE 18(a). NONLINEAR RESPONSE OF TETRACHLOROETHYLENE ON THE ECD

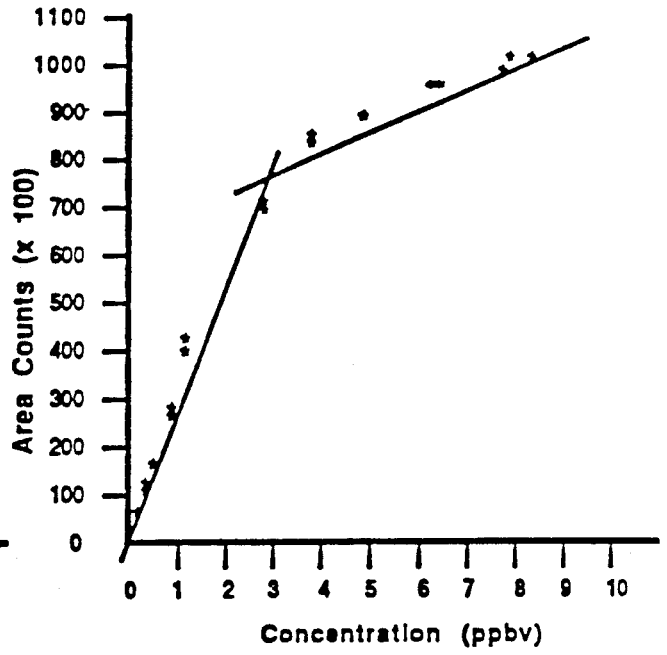


FIGURE 18(b). NONLINEAR RESPONSE OF CARBON TETRACHLORIDE ON THE ECD

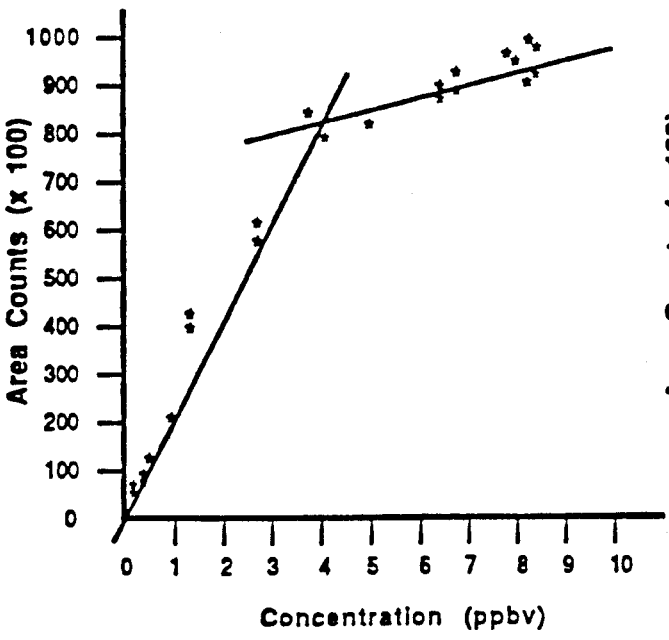


FIGURE 18(c). NONLINEAR RESPONSE OF HEXACHLOROBUTADIENE ON THE ECD

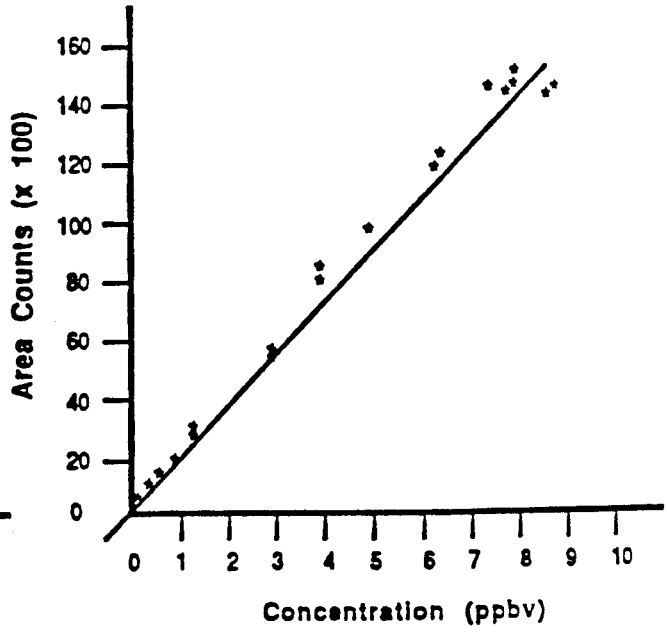


FIGURE 18(d). LINEAR RESPONSE OF CHLOROFORM ON THE ECD

FIGURE 18. RESPONSE OF ECD TO VARIOUS VOCs

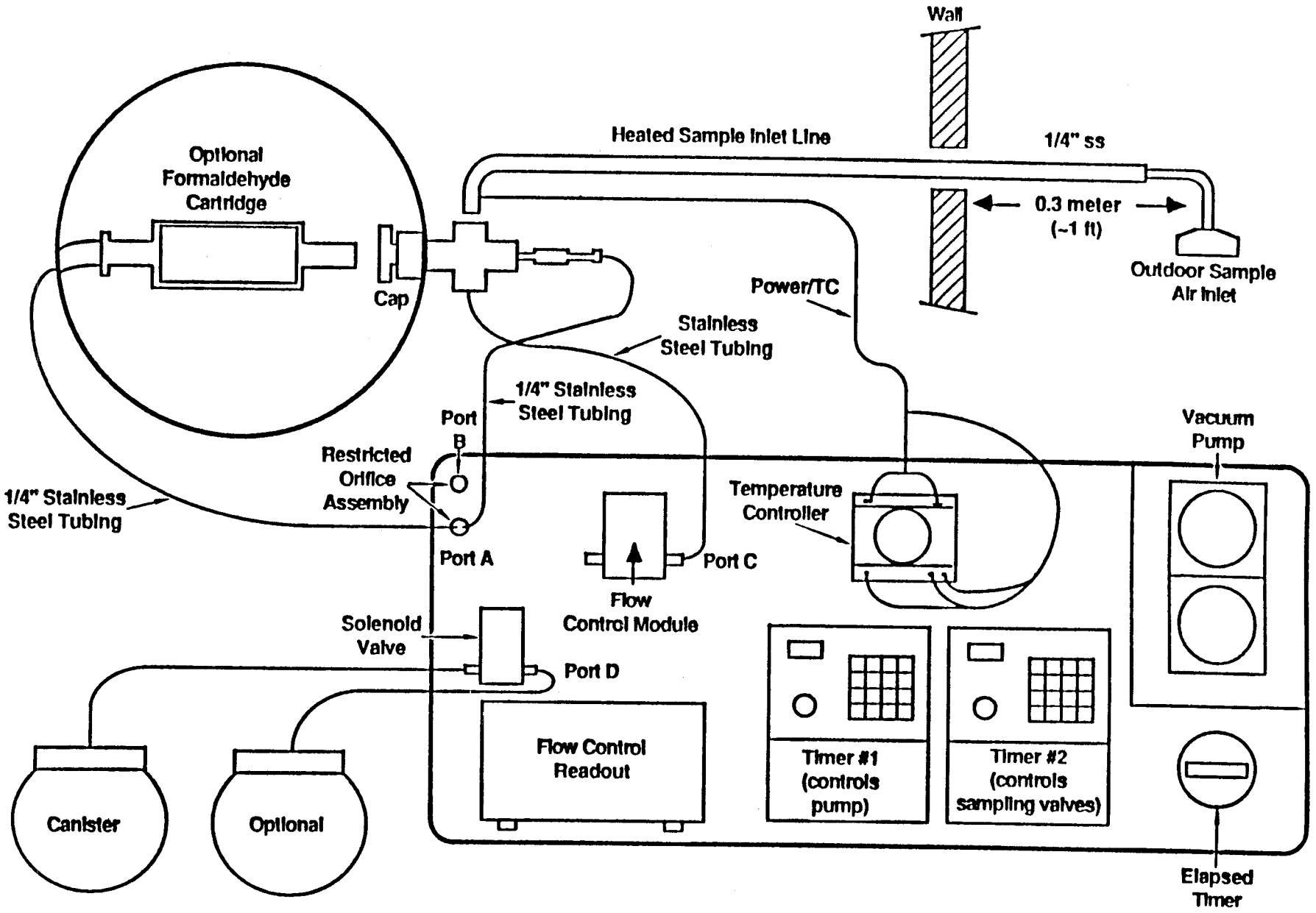


FIGURE 19. U.S. ENVIRONMENTAL PROTECTION AGENCY UATP, SCHEMATIC OF SAMPLE INLET CONNECTIONS SAMPLER

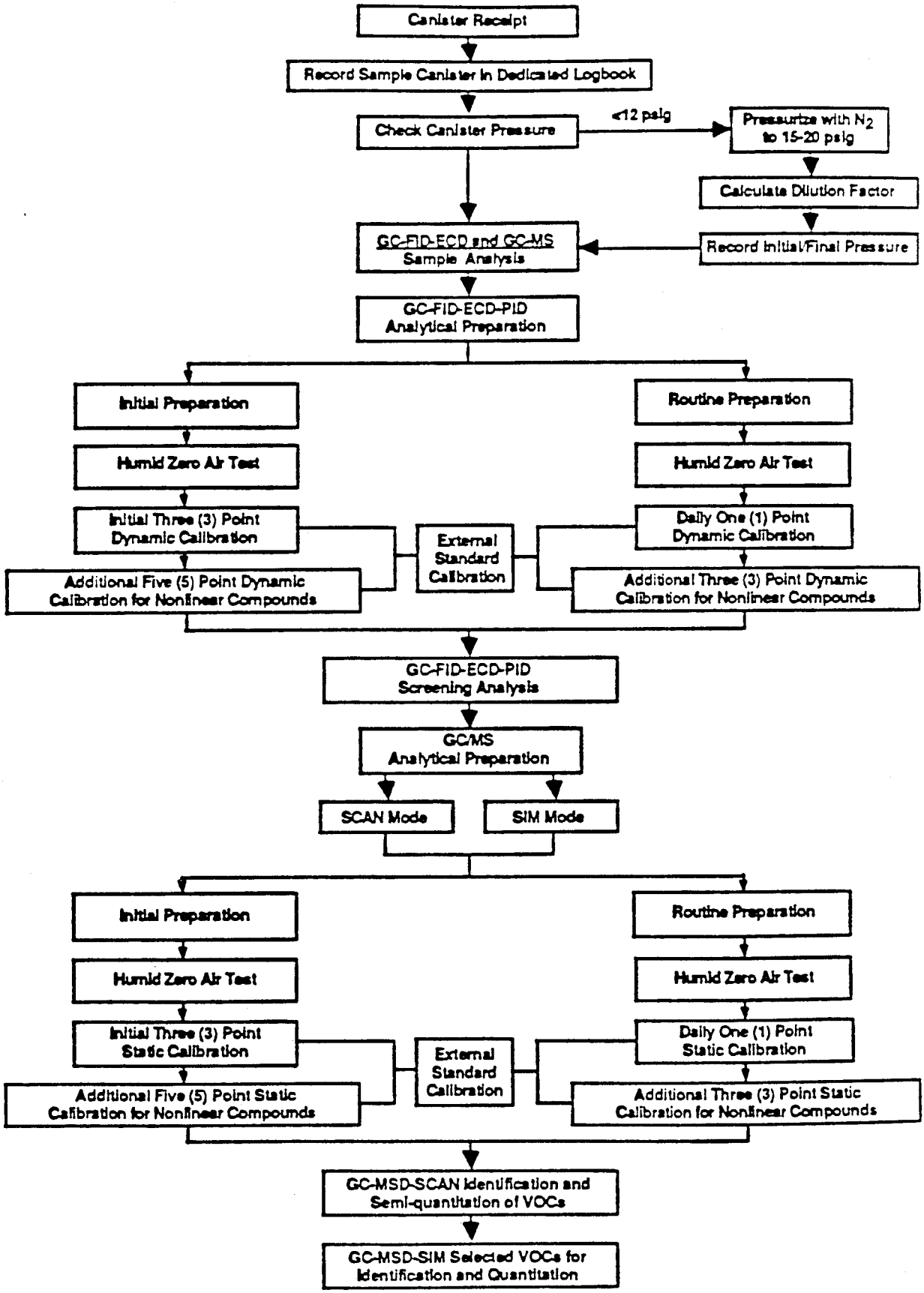

Canister Receipt
Record Sample Canister in Dedicated Logbook
Check Canister Pressure
<12 psig
Pressurize with N_2 to 15-20 psig
Calculate Dilution Factor
Record Initial/Final Pressure
GC-FID-ECD and GC-MS Sample Analysis
GC-FID-ECD-PID Analytical Preparation
Initial Preparation
Humid Zero Air Test
Initial Three (3) Point Dynamic Calibration
Additional Five (5) Point Dynamic Calibration for Nonlinear Compounds
Routine Preparation
Humid Zero Air Test
Daily One (1) Point Dynamic Calibration
Additional Three (3) Point Dynamic Calibration for Nonlinear Compounds
External Standard Calibration
GC-FID-ECD-PID Screening Analysis
GC/MS Analytical Preparation
SCAN Mode
SIM Mode
Initial Preparation
Humid Zero Air Test
Initial Three (3) Point Static Calibration
Additional Five (5) Point Static Calibration for Nonlinear Compounds
Routine Preparation
Humid Zero Air Test
Daily One (1) Point Static Calibration
Additional Three (3) Point Static Calibration for Nonlinear Compounds
External Standard Calibration
GC-MSD-SCAN Identification and Semi-quantitation of VOCs
GC-MSD-SIM Selected VOCs for Identification and Quantitation

FIGURE 20. FLOWCHART OF ANALYTICAL SYSTEMS PREPARATION.

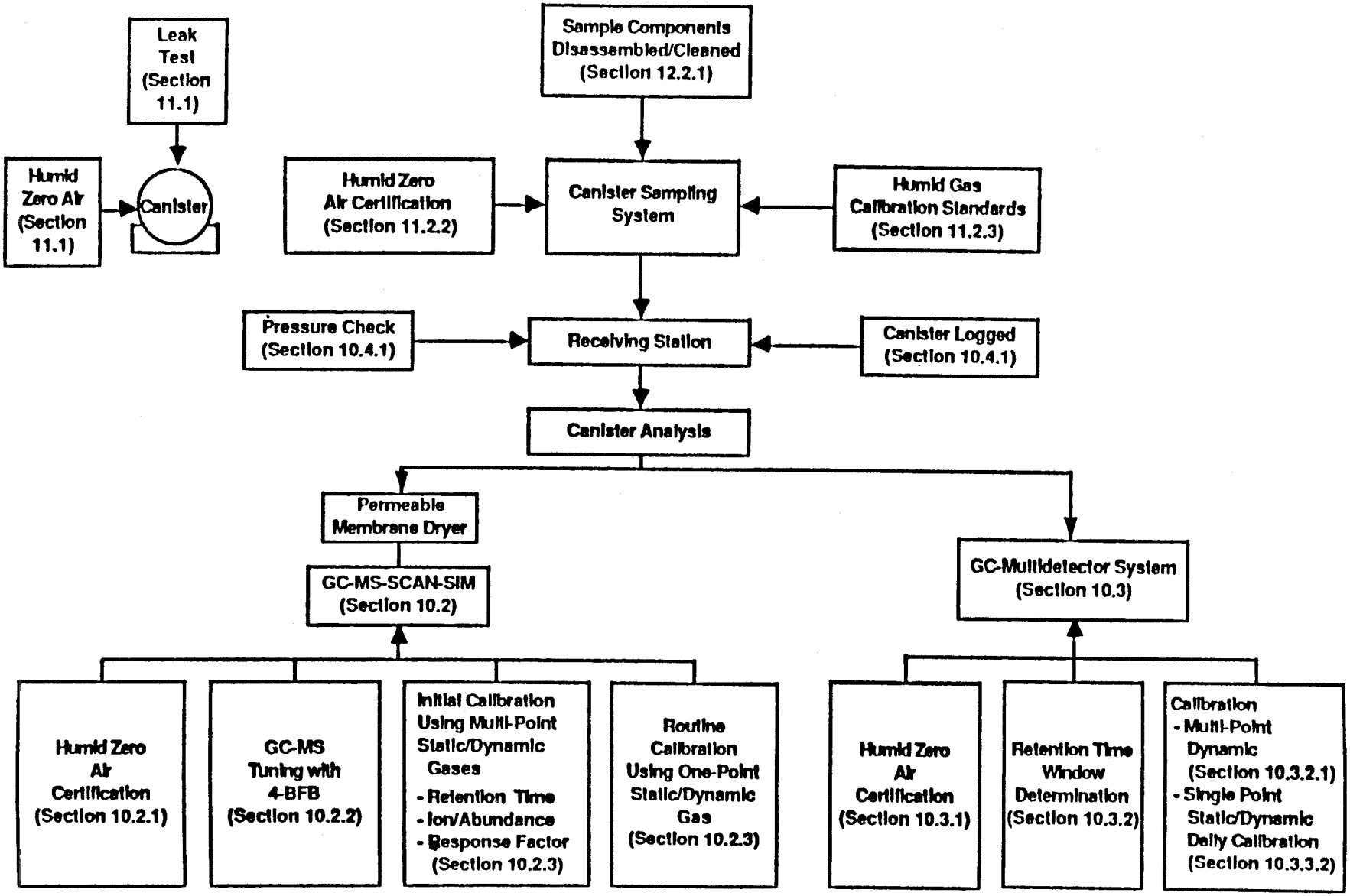

Leak Test (Section 11.1)
Sample Components Disassembled/Cleaned (Section 12.2.1)
Humid Zero Air (Section 11.1)
Canister
Humid Zero Air Certification (Section 11.2.2)
Canister Sampling System
Humid Gas Calibration Standards (Section 11.2.3)
Pressure Check (Section 10.4.1)
Receiving Station
Canister Logged (Section 10.4.1)
Canister Analysis
Permeable Membrane Dryer
GC-MS-SCAN-SIM (Section 10.2)
GC-Multidetector System (Section 10.3)
Humid Zero Air Certification (Section 10.2.1)
GC-MS Tuning with 4-BFB (Section 10.2.2)
Initial Calibration Using Multi-Point Static/Dynamic Gases
- Retention Time
- Ion/Abundance
- Response Factor (Section 10.2.3)
Routine Calibration Using One-Point Static/Dynamic Gas (Section 10.2.3)
Humid Zero Air Certification (Section 10.3.1)
Retention Time Window Determination (Section 10.3.2)
Calibration
- Multi-Point Dynamic (Section 10.3.2.1)
- Single Point Static/Dynamic Daily Calibration (Section 10.3.3.2)

FIGURE 21. SYSTEM QUALITY ASSURANCE / QUALITY CONTROL (QA/QC) ACTIVITIES ASSOCIATED WITH VARIOUS ANALYTICAL SYSTEMS

APPENDIX A

AVAILABILITY OF AUDIT CYLINDERS FROM UNITED STATES ENVIRONMENTAL PROTECTION AGENCY USEPA PROGRAMS/ REGIONAL OFFICES, STATE AND LOCAL AGENCIES AND THEIR CONTRACTORS

1.0 Availability of Audit Cylinders

1.1 The USEPA has available, at no charge, cylinder gas standards of hazardous organic compounds at the ppb level that may be used to audit the performance of indoor air source measurement systems.

1.2 Each audit cylinder contains 5 to 18 hazardous organic compounds in a balance of N_2 gas. Audit cylinders are available in several concentration ranges. The concentration of each organic compound in the audit cylinder is within the range illustrated in Table A-1.

2.0 Audit Cylinder Certification

2.1 All audit cylinders are periodically analyzed to assure that cylinder concentrations have remained stable.

2.2 All stability analyses include quality control analyses of ppb hazardous organic gas standards prepared by the National Bureau of Standards for USEPA.

3.0 Audit Cylinder Acquisition

3.1 USEPA program/regional offices, state/local agencies, and their contractors may obtain audit cylinders (and an audit gas delivery system, if applicable) for performance audits during:

- RCRA Hazardous Waste Trial Burns For PHOC's; and
- Ambient/Indoor Air Measurement of Toxic Organics.

3.2 The audit cylinders may be acquired by contacting:

Robert L. Lampe
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division
MD-77B
Research Triangle Park, NC 27711
919-541-4531

TABLE A-1. AVAILABLE USEPA PERFORMANCE AUDIT CYLINDERS

Group I Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene

Group II Compounds

Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
Acetonitrile
Trichlorofluoromethane (Freon-11)
Dichlorodifluoromethane (Freon-12)
Bromomethane
Methyl ethyl ketone
1,1,1-trichloroethane

Group III Compounds

Pyridine (pyridine in Group III cylinders but certified analysis not available)
Vinylidene chloride
1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113)
1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
Acetone
1-4 Dioxane
Toluene
Chlorobenzene

Group I Ranges

7 to 90 ppb
90 to 430 ppb
430 to 10,000 ppb

Group II Ranges

7 to 90 ppb
90 to 430 ppb

Group III Ranges

70 to 90 ppb
90 to 430 ppb

Group IV

Acrylonitrile
1,3-butadiene
Ethylene oxide
Methylene chloride
Propylene oxide
o-xylene

Group V

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene
Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
1,1,1-trichloroethane
Methylene chloride
Trichlorofluoromethane (Freon-11)
Bromomethane
Toluene
Chlorobenzene
1,3-Butadiene
o-xylene
Ethyl benzene
1,2-dichloropropane

Group IV Ranges

7 to 90 ppb
430 to 10,000 ppb

Group V Ranges

1 to 40 ppb

APPENDIX B

OPERATING PROCEDURES FOR A PORTABLE GAS CHROMATOGRAPH EQUIPPED WITH A PHOTOIONIZATION DETECTOR

1.0 Scope

This procedure is intended to screen ambient air environments for volatile organic compounds. Screening is accomplished by collection of VOC samples within an area and analysis onsite using a portable gas chromatograph/integrator (Photovac Models 10S10, 10S50) or equivalent. This procedure is not intended to yield quantitative or definite qualitative information regarding the substances detected. Rather, it provides a chromatographic "profile" of the occurrence and intensity of unknown volatile compounds which assists in placement of fixed-site samplers.

2.0 Applicable Documents

2.1 ASTM Standards

E260 - Recommended Practice for General Gas Chromatography Procedures

E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Portable Instruments User's Manual for Monitoring VOC Sources, EPA-34011-86-015, U.S. Environmental Protection Agency, Washington, DC, June, 1986.

3.0 Summary of Method

3.1 An air sample is extracted directly from ambient air and analyzed on-site by a portable GC.

3.2 Analysis is accomplished by drawing an accurate volume of ambient air through a sampling port and into a concentrator, then the sample air is transported by carrier gas onto a packed column and into a PID, resulting in response peak(s). Retention times are compared with those in a standard chromatogram to predict the probable identity of the sample components.

4.0 Significance

4.1 VOCs are emitted into the atmosphere from a variety of sources including petroleum refineries, synthetic organic chemical plants, natural gas processing plants, and automobile exhaust. Many of these VOC emissions are acutely toxic; therefore, their determination in indoor air is necessary to assess human health impacts.

4.2 Conventional methods of VOC determination use solid sorbent and canister sampling techniques.

4.3 Collection of indoor air samples in canisters provides (1) convenient integration of embient samples over a specific time period, (e.g., 24 hours); (2) remote sampling and central analysis; (3) ease of storing and shipping samples, if necessary; (4) unattended sample collection; (5) analysis of samples from multiple sites with one analytical system; and (6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems.

4.4 The use of portable GC equipped with multidetectors has assisted air toxics programs by using the portable GC as a "screening tool" to determine "hot spots," potential interferences, and semiquantitation of VOCs/SVOCs, prior to locating more traditional fixed-site samplers.

5.0 Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. Abbreviations and symbols pertinent to this method are defined at point of use.

6.0 Interferences

6.1 The most significant interferences result from extreme differences in limits of detection (LOD) among the target VOCs (Table B-1). Limitations in resolution associated with ambient temperature, chromatography and the relatively large number of chemicals result in coelution of many of the target components. Coelution of compounds with significantly different PID sensitivities will mask compounds with more modest sensitivities. This will be most dramatic in interferences from benzene and toluene.

6.2 A typical chromatogram and peak assignments of a standard mixture of target VOCs (under the prescribed analytical conditions of this method) are illustrated in Figure B-1. Samples which contain a highly complex mixture of components and/or interfering levels of benzene and toluene are analyzed on a second, longer chromatographic column. The same liquid phase in the primary column is contained in the alternate column but at a higher percent loading.

6.3 Recent designs in commercially available GCs (Table B-2) have preconcentrator capabilities for sampling lower concentrations of VOCs, pre-column detection with back-flush capability for shorter analytical time, constant column temperature for method precision and accuracy and multidetector (PID, ECD, and FID) capability for versatility. Many of those newer features address the weaknesses and interferences mentioned above.

7.0 Apparatus

7.1 Gas chromatograph. A GC (Photovac Inc., 739 8 Parks Ave, Huntington, NY, 11743, Model 10S10 or 10S50), or equivalent used for surveying ambient air environments (which could employ a multidetector) for sensing numerous VOCs compounds eluting from a packed column at room temperatures. This particular portable GC procedure is written employing the photoionization detector as its major sensing device, as part of the Photovac Model 10S10 portable GC survey tool. Chromatograms are developed on a columm of 3% SP-2100 on 100/120 Supelcoport (0.65 m x 3.2 mm I.D.) with a flow of 30 cm^3/min air.

7.2 GC accessories. In addition to the basic gas chromatograph, several other pieces of equipment are required to execute the survey sampling. Those include gas-tight syringes for standard injection, alternate carrier gas supplies, high pressure connections for filling the internal carrier gas reservoir, and if the Model 10S10 is used, a recording integrator (Hewlett Packard, Avondale, PA, Model 3390A), or equivalent.

8.0 Reagents and Materials

8.1 Carrier gas. "Zero" air [<0.1 ppm total hydrocarbon (THC)] is used as the carrier gas. This gas is conveniently contained in 0.84 m3 (30 ft^3) aluminum cylinders. Carrier gas of poorer quality may result in spurious peaks in sample chromatograms. A Brooks, Type 1355.00F1AAA rotameter (or equivalent) with an R-215-AAA tube and glass float is used to set column flow.

8.2 System performance mixture. A mixture or three target compounds (e.g., benzene, trichloroethylene, and styrene) in nitrogen is used for monitoring instrument performance. The approximate concentration for each of the compounds in this mixture is 10 parts per billion (ppb). This mixture is manufactured in small, disposable gas cylinders [at 275 kPa (40 psi)] from Scott Specialty Gases, or equivalent.

8.3 Reagent grade nitrogen gas. A small disposable cylinder of high purity nitrogen gas is used for blank injections.

8.4 Sampling syringes. Gas-tight syringes, without attached shut-off valves (Hamilton Model 1002LT), or equivalent are used to introduce accurate sample volumes into the high pressure injectors on the portable gas chromatograph. Gas syringes with shut-off valves are not recommended because of memory problems associated with the valves. For samples suspected of containing high concentrations of volatile compounds, disposable glass syringes (e.g, Glaspak, or equivalent) with stainless steel/Teflon® hub needles are used.

8.5 High pressure filler. An adapter (Photovac SA101, or equivalent) for filling the internal carrier gas reservoir on the portable GC is used to deliver "zero" air.

9.0 Procedure

9.1 Instrument Setup

9.1.1 The portable gas chromatograph must be prepared prior to use in the ambient survey sampling. The pre-sampling activities consist of filling the internal carrier gas cylinder, charging the internal power supply, adjusting individual column carrier gas flows, and stabilizing the photoionization detector.

9.1.2 The internal reservoir is filled with "zero" air. The internal 12V, 6AH lead/acid battery can be recharged to provide up to eight hours of operation. A battery which is discharged will automatically cause the power to the instrument to he shut down and will require an overnight charge. During AC operation, the batteries will automatically be trickle-charged or in a standby mode.

9.1.3 The portable GC should be operated (using the internal battery power supply) at least forty minutes prior to collection of the first sample to insure that the photoionzation detector has stabilized. Upon arriving at the area to be sampled, the unit should be connected to AC power, if available.

9.2 Sample Collection

9.2.1 After the portable gas chromatograph is located and connected to 110V AC, the carrier gas flows must be adjusted. Flows to the 1.22 meter, 5% SE-30 and 0.66 meter, 3% SP2100 columns are adjusted with needle valves. Flows of 60 cm^3/min (5% SE-30) and 30 cm^3/min (3% SP2100) are adjusted by means of a calibrated rotameter. Switching between the two columns is accomplished by turning the valve located beneath the electronic module. During long periods of inactivity, the flows to both columns should be reduced to conserve pressure in the internal carrier gas supply. The baseline on the recorder/integrator is set to 20% full scale.

9.2.2 Prior to analysis of actual samples, an injection of the performance evaluation mixture must be made to verify - chromatographic and detector performance. This is accomplished by withdrawing 1.0 mL samples of this mixture from the calibration cylinder and injecting it onto the 3% SP2100 column. The next sample analyzed should be a blank, consisting of reagent grade nitrogen.

9.2.3 Ambient air samples are injected onto the 3% SP2100 column. The chromatogram is developed for 15 minutes. Samples which produce particularly complex chromatograms, especially for early eluting components, are reinjected on the 5% SE-30 column. [Note: In no instance should a syringe which has been used for the injection of the calibrant/system performance mixture be used for the acquisition and collection of samples, or vice versa.]

9.2.4 Samples have generally been collected from the ambient air at sites which are near suspected sources of VOCs and SVOCs and compared with those which are not. Typically, selection of sample locations is based on the presence of chemical odors. Samples collected in areas without detectable odors have not shown significant PID responses. Therefore, sampling efforts should be initially concentrated on "suspect" environments (i.e., those which have appreciable odors). The objective of the sampling is to locate sources of the target compounds. Ultimately, samples should be collected throughout the entire location, but with particular attention given to areas of high or frequent occupation.

9.3 Sample Analysis

9.3.1 Qualitative analysis. Positive identification of sample components is not the objective of this "screening" procedure. Visual comparison of retention times to those in a standard chromatogram (Figure B-1) are used only to predict the probable sample component types.

9.3.2 Estimation of levels. As with qualitative analysis, estimates of component concentrations are extremely tentative and are based on instrument responses to the calibrant species (e.g., benzene, trichloroethylene, styrene), the proposed component identification, and the difference in response between sample component and calibrant. For purposes of locating pollutant emission sources, roughly estimated concentrations and suspected compound types are considered sufficient.

10.0 Performance Criteria and Quality Assurance

Required quality assurance measures and guidance concerning performance criteria that should be achieved within each laboratory are summarized and provided in the following section.

10.1 Standard Operating Procedures

10.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: (l) assembly, calibration, leak check, and operation of the specific portable GC sampling system and equipment used; (2) preparation, storage, shipment, and handling of the portable GC sampler; (3) purchase, certification, and transport of standard reference materials; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

10.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the survey work.

10.2 Quality Assurance Program

10.2.1 Reagent and materials control. The carrier gas employed with the portable GC is "zero air" containing less than 0.1 ppm VOCs. System performance mixtures are certified standard mixtures purchased from Scott Specialty Gases, or equivalent.

10.2.2 Sampling protocol and chain of custody. Sampling protocol sheets must be completed for each sample. Specifics of the sample with regard to sampling location, sample volume, analysis conditions, and supporting calibration and visual inspection information are detailed by these documents. An example form is exhibited in Table B-3.

10.2.3 Blanks, Duplicates, and System Performance Samples

10.2.3.1 Blanks and Duplicates. Ten percent of all injections made to the portable GC are blanks, where the blank is reagent grade nitrogen gas. This is the second injection in each sampling location. An additional 10% of all injections made are duplicate injections. This will enhance the probability that the chromatogram of a sample reflects only the composition of that sample and not any previous injection. Blank injections showing a significant amount of contaminants will be cause for remedial action.

10.2.3.2 System Performance Mixture. An injection of the system performance mixture will be made at the beginning of a visit to a particular sampling location (i.e., the first injection). The range of acceptable chromatographic system performance criteria and detector response is shown in Table B-4. These criteria are selected with regard to the intended application of this protocol and the limited availability of standard mixtures in this area. Corrective action should be taken with the column or PID before sample injections are made if the performance is deemed out-of-range. Under this regimen of blanks and system performance samples, approximately eight samples can be collected and analyzed in a three hour visit to each sampling location.

10.3 Method Precision and Accuracy

The purpose of the analytical approach outlined in this method is to provide presumptive information regarding the presence of selected VOCs and SVOCs emissions. In this context, precision and accuracy are to be determined. However, quality assurance criteria are described in Section 10.2 which insure the samples collected represent the indoor environment.

10.4 Range and Limits of Detection

The range and limits of detection of this method are highly compound dependent due to large differences in response of the portable GCs photoionization detector to the various target compounds. Aromatic compounds and olefinic halogenated compounds will be detected at lower levels than the halomethanes or aliphatic hydrocarbons. The concentration range of application of this method is approximately two orders of magnitude.

TABLE B-1

ESTIMATED LIMITS OF DETECTION (LOD) FOR SELECTED VOCs BASED ON 1 uL SAMPLE VOLUME

Compound	LOD (ng)	LOD (ppb)
Chloroform[a]	2	450
1,1,1-Trichloroethane[a]	2	450
Carbon tetrachloride[a]	2	450
Benzene	.006	2
1,2-Dichloroethane[b]	.05	14
Trichloroethylene[b]	.05	14
Tetrachloroethylene[b]	.05	14
1,2-Dibromoethane	.02	2
p-Xylene[c]	.02	4
m-Xylene[c]	.02	4
o-Xylene[d]	.01	3
Styrene[d]	.01	3

[a]Chloroform, 1,1,1-Trichloroethane, and Carbon tetrachloride coelute on 0.66 m 3% SP2100.

[b]1,2-Dichloroethane, Tricholroethylene, and Tetrachloroethylene coelute on 0.66 m 3% SP2100.

[c]p-Xylene and m-Xylene coelute on 0.66 m 3% SP2100.

[d]Styrene and o-Xylene coelute on 0.66 m 3% SP2100.

TABLE B-2

COMMERCIALLY AVAILABLE PORTABLE VOC DETECTION INSTRUMENTS

Monitor	Detection Principle	Range ppm	Sensitivity	Response Time, s	Accessories	Calibration Techniques	Weaknesses	Service Rate	Lack of Response	Cost, $	sample Waste L/m
550,551 555,580 (AID, Inc.)	FID FID	0-200, 0-2000, 0-10,000	0.1 ppm at 0-200 ppm	< 5		• Bag sampling	• Umbilical cord too short • Ditigal readout hard to read • Flame out frequently	8 hrs.		$4,300	1.5
OVA 108, 128 Century Systems, Inc. (Foxboro)	FID	0-10, 0-100, 0-1000, 0-10,000, 0-100,000	0.2 ppm (Model 128) 0.5 ppm (Model 108)	2 2	• Thermal Desorbers available • Optional GC available	• Hand Space • Direct Injection • Bag Sample	• Battery failure • Sample line kinks • Compounds containing O_2/M give low response • Negative Response to CO/CO_2	8 hrs.		6,300	
F1-101 (MMU Systems, Inc.	FID	1 1-20 1-200 1-2000	0.1 pm Low molecular weight aromatics	< 5	• Three lamps available • 9.5 (aromatics) • 10.2 (2-4 compounds) • 11.7 (halocarbons)	• External Gas Cyl. • Bag Sample	• Three lamps - may miss something	10 hrs.	• C1 hydrocarbons • CH_4	4,955	0.5
TLV Sniffer (Bacharach)	Catalytic combustion	0-500 0-5000	2.0 ppm	5		• Bag Sample • Head Space • Bag Sample	• Change in gas temperature/humidity affects response			900	
Ecolyzer 400 (Energistics Science)	Catalytic combustion	0-50,000 0-100% LFL	1%	15							
Miran IA (Foxboro)	IR	ppm to %	1 ppm	1,4,10 and 40						9,500	
Miran 1B (Foxboro)	IR	ppm to %								12,500	
Scentor (Sentex)	GC/EC, Argon Ionization PID		0.01 ppb C1 organics	2	Preconcentration for Thermal Desorption GC Columns Auto Calibration from Integral Gas Cylinder	• Internal gas cycle • Preconcentrator • GC Column				12,950	
Photovac - Standard Automatic Computer Auto Comp. Communication	PID (UV Light)	0	0.1 ppb Benzene with signal-to-noise ratio 4:1, Good for aromatics	2	• Dual Column • Manual/Auto Injection • Column Cond. • Pre-flush • Auto Dial Modes		• Column operates at ambient temp. • STD in lab then to field at diff. temp. • Can't inject liquid sample • Light fractions interferer		• H2O • O2	6,995 8,995 10,500 10,955 12,955	
Photovac Tip	PID	0-2000 ppm	0.05 ppm Benzene	3							

TABLE B-3

PORTABLE GAS CHROMATOGRAPH SAMPLING SHEET

DATE: _____ LOCATION: _____ TIME: _____

CHROMATOGRAPHIC CONDITIONS: _____

COLUMN 1: COLUMN TYPE:

I.D. (mm): _____ LENGTH (mm): _____ FLOW (mL/min): _____

COLUMN 2: COLUMN TYPE:

I.D. (mm): _____ LENGTH (mm): _____ FLOW (mL/min): _____

INJ. NO.	INJ. VOL.	COLUMN NO.	SETTING	LOCATION

SITE PLAN (indicate sampling locations):

_____ _____

DATE **SIGNATURE**

TABLE B-4

SYSTEM PERFORMANCE CRITERIA FOR PORTABLE GC[a]

Criteria	Test Compound	Acceptable Range	Suggested Corrective Action
PID Response	Trichloroethylene	$\geq 10^8$uV-sec/ng	Re-tune or replace lamp
Elution Time	Styrene	2.65 ± 0.15 min	Inspect for leaks, adjust carrier flow
Resolution[b]	Benzene/Trichloroethylene	≥ 1.4	Replace column

[a]Based on analysis of a vapor mixture of benzene, styrene, and trichloroethylene.

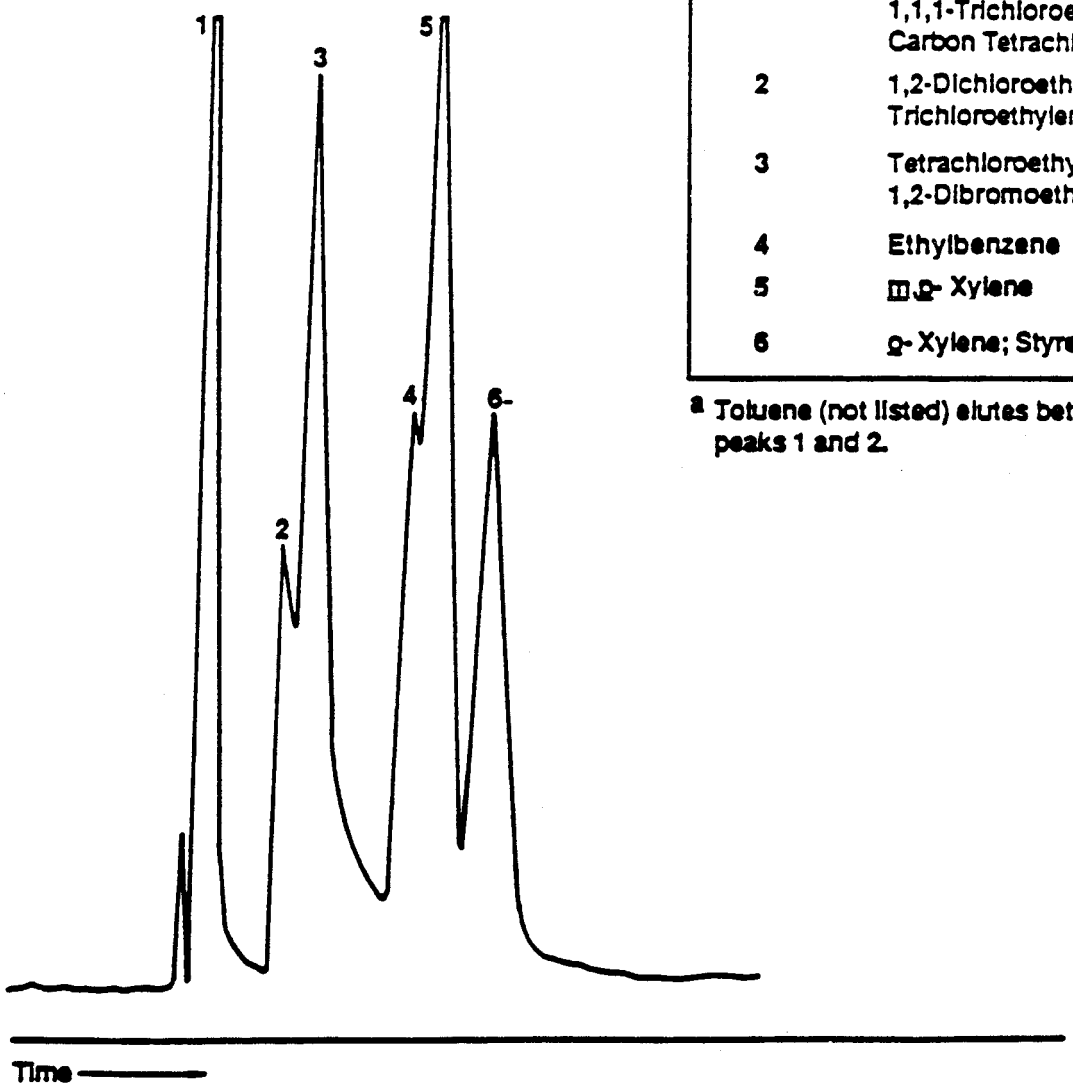
[b]Define by: $R+ = 2d/(W_1 + W_2)$; where d = distance between the peaks and W = peak width at base.

TABLE B-5

ESTIMATED LIMITS OF DETECTION (LOD) FOR SELECTED VOCs

Compound	LOD (ng)	LOD (ppb)
Chloroform[a]	2	450
I, I, I-Trichloroethane[a]	2	450
Carbon tetrachloride[a]	2	450
Benzene	.006	2
1,2-Dichloroethane[b]	.05	14
Trichloroethylene[b]	.05	14
Tetrachloroethylene[b]	.05	14
1,2-Dibromoethane	.02	2
p-Xylene[c]	.02	4
m-Xylene[c]	.02	4
o-Xylene[d]	.01	3
Styrene[d]	.01	3

[a]Chloroform, I, I, I-Trichloroethane, and Carbon tetrachloride coelute on 0.66 m 3% SP2100.
[b]1,2-Dichloroethane, Trichloroethylene, and Tetrachloroethylene coelute on 0.66 m 3% SP2100.
[c]p-Xylene and m-Xylene coelute on 0.66 m 3% SP2100.
[d]Styrene and o-Xylene coelute on 0.66 m 3% SP2100.



Peak Assignments For Standard Mixture

Peak No.	Compound(s) [a]
1	Benzene; Chloroform; 1,1,1-Trichloroethane; Carbon Tetrachloride
2	1,2-Dichloroethane; Trichloroethylene
3	Tetrachloroethylene; 1,2-Dibromoethane
4	Ethylbenzene
5	m,p- Xylene
6	o- Xylene; Styrene

[a] Toluene (not listed) elutes between peaks 1 and 2.

FIGURE B-1. TYPICAL CHROMATOGRAM OF VOCs DETERMINED BY A PORTABLE GC

APPENDIX C

INSTALLATION AND OPERATION PROCEDURES FOR U.S. ENVIRONMENTAL PROTECTION AGENCY'S URBAN AIR TOXIC POLLUTANT PROGRAM SAMPLER

1.0 Scope

1.1 The subatmospheric sampling system described in this method has been modified and redesigned specifically for use in USEPA's Urban Air Toxic Pollutant Program (UATP), a joint project of USEPA's Office of Air Quality Planning and Standards, the Environmental Monitoring Systems Laboratory, and the participating state air pollution control agencies. The purpose of UATP is to provide analytical support to the states in their assessment of potential health risks from certain toxic organic compounds that may be present in urban atmospheres. The sampler is described in the paper, "Automatic Sampler for Collection of 24-Hour Integrated Whole-Air Samples for Organic Analysis," to be presented at the 1988 Annual Meeting of APCA, Dallas, Texas, June, 1988 (Paper No. 88-150.3).

1.2 The sampler is based on the collection of whole air samples in 6-liter, SUMMA® passivated stainless steel canisters. The sampler features electronic timer for ease, accuracy and flexibility of sample period programming, an independently setable presample warm-up and ambient air purge period, protection from loss of sample due to power interruptions, and a self-contained configuration housed in an all-metal portable case, as illustrated in Figure C-1.

1.3 The design of the sampler is pumpless, using an evacuated canister to draw the ambient sample air into itself at a fixed flow rate (3-5 cm^3/min) controlled by an electronic mass flow controller. Because of the relatively low sample flow rates necessary for the integration periods, auxiliary flushing of the sample inlet line is provided by a small, general-purpose vacuum pump (not in contact with the sample air stream). Further, experience has shown that inlet lines and surfaces sometimes build up or accumulate substantial concentrations of organic materials under stagnant (zero flow rate) conditions. Therefore such lines and surfaces need to be purged and equilibrated to the sample air for some time prior to the beginning of the actual sample collection period. For this reason, the sampler includes dual timers, one of which is set to start the pump several hours prior to the specified start of the sample period to purge the inlet lines and surfaces. As illustrated in Figure C-1 sample air drawn into the canister passes through only four components: the heated inlet line, a 2-micron particulate filter, the electron flow controller, and the latching solenoid valve.

2.0 Summary of Method

2.1 In operation, timer #1 is set to start the pump about 6 hours before the scheduled sample period. The pump draws sample air in through the sample inlet and particulate filter to purge and equilibrate these components, at a flow rate limited by the capillary to approximately 100 cm^3/min. Timer 1 also energizes the heated inlet line to allow it to come up to its controlled temperature of 65 to 70 degrees C, and turns on the flow controller to allow it to stabilize. The pump draws additional sample air through the flow controller by way of the normally open port of the 3-way solenoid valve. This flow purges the flow controller and allows it to achieve a stable controlled flow at the specified sample flow rate prior to the sample period.

2.2 At the scheduled start of the sample period, timer #2 is set to activate both solenoid valves. When activated, the 3-way solenoid valve closes its normally open port to stop the flow controller purge flow and opens its normally closed port to start flow through the aldehyde sample cartridges. Simultaneously, the latching solenoid valve opens to start sample flow into the canister.

2.3 At the end of the sample period, timer #2 closes the latching solenoid valve to stop the sample flow and seal the sample in the canister and also de-energizes the pump, flow controller, 3-way solenoid, and heated inlet line. During operation, the pump and sampler are located external to the sampler. The 2.4 meter (8 foot) heated inlet line is installed through the outside wall, with most of its length outside and terminated externally with an inverted glass funnel to exclude precipitation. The indoor end is terminated in a stainless steel cross fitting to provide connections for the canister sample and the two optional formaldehyde cartridge samples.

3.0 Sampler Installation

3.1 The sampler must be operated indoors with the temperature between 20-32°C (68 to 90°F). The sampler case should be located conveniently on a table, shelf, or other flat surface. Access to a source of 115 vac line power (500 watts min) is also required. The pump is removed from the sampler case and located remotely from the sampler (connected with a 1/4 inch O.D. extension tubing and a suitable electrical extension cord).

3.2 Electrical Connections (Figure C-1)

3.2.1 The sampler cover is removed. The sampler is not plugged into the 115 vac power until all other electrical connections are completed.

3.2.2 The pump is plugged into its power connector (if not already connected) and the battery connectors are snapped onto the battery packs on the covers of both timers.

3.2.3 The sampler power plug is inserted into a 115 volts ac line grounded receptacle. The sampler must be grounded for operator safety. The electrical wires are routed and tied so they remain out of the way.

3.3 Pneumatic Connections

3.3.1 The length of 1/16 inch O.D. stainless steel tubing is connected from port A of the sampler (on the right side of the flow controller module) to the air inlet line.

3.3.2 The pump is connected to the sampler with 1/4 inch O.D. plastic tubing. This tubing may be up to 7 meters (20 feet) long. A short length of tubing is installed to reduce pump noise. All tubing is conveniently routed and, if necessary, tied in place.

4.0 Sampler Preparation

4.1 Canister

4.1.1 The sample canister is installed no more than 2 days before the scheduled sampling day.

4.1.2 With timer #1 ON, the flow controller is allowed to warm up for at least 15 minutes, longer if possible.

4.1.3 An evacuated canister is connected to one of the short lengths of 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) of the sampler. The canister valve is left closed. The Swagelok fitting on the canister must not be cross-threaded. The connection is tightened snugly with a wrench.

4.1.4 The end of the other length of stainless steel tubing from port B (solenoid valve) is connected with a Swagelok plug.

4.1.5 If duplicate canisters are to be sampled, the plug is removed from the second 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) and the second canister is connected. The canister valve is left closed.

4.1.6 The ON button of timer #2 is pressed. The flow through the flow controller should be stopped by this action.

4.1.7 The flow controller switch is turned to "READ" and the zero flow reading is obtained. If this reading is not stable, wait until the reading is stabilized.

4.1.8 The flow controller switch is turned to "SET" and the flow setting is adjusted to the algebraic SUM of the most recent entry on Table C-1 and the zero reading obtained in step 4.1.7 (If the zero reading is negative, SUBTRACT the zero reading from the Table C-1 value). Be sure to use the correct Table C-1 flow value for one or two canisters, as appropriate. [Note: If the analytical laboratory determines that the canister sample pressure is too low or too high, a new flow setting or settings will be issued for the sampler. The new flow setting should be recorded in Table C-1 and used until superseded by new settings.]

4.1.9 Timer #2 is turned OFF to again start the flow through the flow controller. With the pump (timer #1) ON and the sampling valve (timer #2) OFF, the flow controller is turned to "READ" and the flow is verified to be the same as the flow setting made in step 4.1.8. If not, the flow setting is rechecked in step 4.1.8 and the flow setting is readjusted if necessary.

4.1.10 The OFF button of timer #1 is pressed to stop the pump.

4.1.11 The canister valve(s) are fully opened.

4.2 Timers

4.2.1 Timer #2 is set to turn ON at the scheduled ON time for the sample period, and OFF at the scheduled OFF time. (See the subsequent section on setting the timers.)

Normal ON time: 12:00 AM on the scheduled sampling day.

Normal OFF time: 11:59 PM on the scheduled sampling day.

(The OFF time is 11:59 PM instead of 12:00 AM so that the day number for the OFF time is the same as the day number for the ON time.) Be sure to set the correct day number.

4.2.2 Timer #1 is set to turn ON six (6) hours before the beginning of the scheduled sample period and OFF at the scheduled OFF time for the sample period (same OFF time as for timer #2). (See the subsequent section on setting the timers.)

Normal ON time: 06:00 PM on the day prior to the scheduled sampling day.
Normal OFF time: 11:59 PM on the scheduled sampling day.

[Note: The timers are wired so that the pump will be on whenever either timer is on. Thus the pump will run if timer #2 is ON even if timer #1 is OFF.]

4.2.3 The elapsed time meter is set to 0.

4.3 Sampler Check

4.3.1 The following must be verified before leaving the sampling site:

(1) Canister(s) is (are) connected properly and the unused connection is capped if only one canister is used.
(2) Canister valve(s) is (are) opened.
(3) Both timers are programmed correctly for the scheduled sample period.
(4) Both timers are set to "AUTO".
(5) Both timers are initially OFF.
(6) Both timers are set to the correct current time of day and day number.
(7) Elasped time meter is set to 0.

4.4 Sampler Recovery (Post Sampling)

4.4.1 The valve on the canister is closed.

4.4.2 The canister is disconnected from the sampler, the sample data sheet is completed, and the canister is prepared for shipment to the analytical laboratory.

4.4.3 If two canisters were sampled, step 2.4.2 is repeated for the other canister.

5.0 Timer Setting

Since the timers are 7-day timers, the days of the week are numbered from 1 to 7. The assignment of day numbers to days of the week is indicated on the timer keypad: 1 = Sunday, 2 = Monday, 3 = Tuesday, 4 = Wednesday, 5 = Thursday, 6 = Friday, and 7 = Saturday. This programming is quite simple, but some timers may malfunction or operate erratically if not programmed exactly right. To assure correct operation, the timers should be reset and completely reprogrammed "from scratch" for each sample. The correct current time of day is re-entered to reprogram the timer. Any program in the timer's memory is erased by resetting the timer (pressing the reset button). The timer is set by the following:

(1) pressing the reset button,
(2) entering the correct day number and time of day,
(3) entering the ON and OFF times for the sample period, and
(4) verifying that the ON and OFF time settings are correct.

5.1 Timer Reset

The timer reset button is pressed, which is recessed in a small hole located just above the LED (light emitting diode) indicator light. A small object that will fit through the hole, such as a pencil, match, or pen is used to press the timer. After reset, the timer display should show | 1 | | 10:00 |. [Note: The timers may operate erratically when the batteries are discharged, which happens when the sampler is unplugged or without power for several hours. When the sampler is again powered up, several hours may be required to recharge the batteries. To avoid discharging the batteries, the battery pack should be disconnected from the timer when the sampler is unplugged.]

5.2 Date and Time Entry

The selector switch is turned to SET and the number button corresponding to the day number is pressed. (For example, a "2" is pressed for Monday.) The current time of day is entered. (For example, if the time is 9:00 AM, 900 is pressed.) AM or PM is pressed as applicable. (Display should show | 2 | | '9:00 | for 9:00 AM Monday.) [Note: ' indicates AM and indicates PM.] The CLOCK button is pressed. (Display should show | - | | —:— |) If an error is made, | E | | EE:EE | is shown on the display. The CLEAR button is pressed and the above steps are repeated. The selector switch is turned to AUTO or MAN to verify correct time setting.

5.3 ON and OFF Entry

The selector switch is turned to SET. The ON and OFF program is entered in the following order: day, number, time, AM or PM, ON or OFF. (Example: To turn ON at 12:00 AM on day 5 (Thursday);, 5, 1200, AM, ON is entered). (Example: To turn OFF at 11:59 PM on day 5 (Thursday), 5, 11:59, PM, OFF is entered.) If the display indicates an error (| E | | EE:EE |), the timer is reset. The selector switch is turned to AUTO.

5.4 ON and OFF Verification

5.4.1 The selector switch is turned to REVIEW. The number of the scheduled sample day is pressed. ON is pressed. The display should show the time of the beginning of the sample period (for example, | 5 | | '12:00 |). [' indicates AM.] ON is pressed again. The display should show | 5 | | —:— | , indicating no other ON times are programmed.

5.4.2 OFF is pressed. The display should show the time of the end of the sample period, (for example, | 5 | , | 11:59 |). PM is indicated by the "," mark before the time. OFF is pressed again. The display should show | 5 | | —:— |, indicating no other OFF times are programmed. The selector is switched to AUTO. If anything is incorrect, the timer is reset and reprogrammed.

TABLE C-1

NET FLOW CONTROLLER SETTING

DATE	1 CANISTER	2 CANISTERS

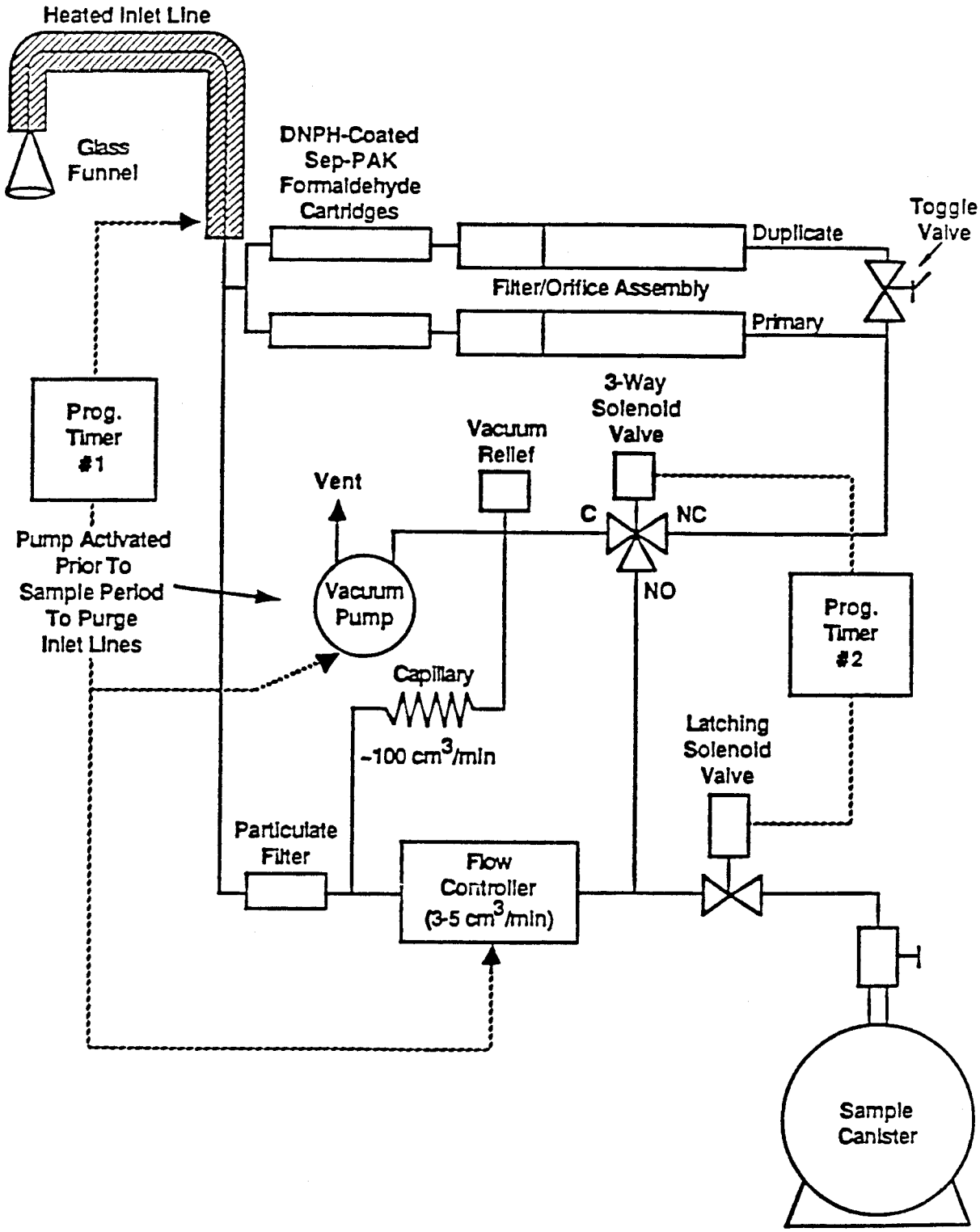


FIGURE C-1. U.S. ENVIRONMENTAL PROTECTION AGENCY UATP SAMPLER SCHEMATIC OF SAMPLE INLET CONNECTIONS

STANDARD OPERATING PROCEDURE FOR METEOROLOGICAL STATION OPERATIONS AND CALIBRATION

STANDARD OPERATING PROCEDURE FOR METEOROLOGICAL STATION OPERATIONS AND CALIBRATION

PURPOSE

The purpose of this document is to provide Standard Operation Procedures (SOPs) for implementation of meteorological station calibration and operations.

APPLICABILITY

This Standard Operation Procedures (SOPs) section is applicable to the operation/calibration of the meteorological station and the collection of meteorological data.

DEFINITIONS

There is no specialized terminology used in these procedures that requires definition beyond the conventional meaning of the terms.

REFERENCES

Manufacturers' Operation and Maintenance Manuals.

DISCUSSION

The station will be operated on a full time basis. The meteorological data at the location are representative of overall site conditions. The weather station also includes an automated data processor which provides 15-minute and 1-(one)-hour data averages. The averaged data is recorded on cassette tapes. Realtime instantaneous data is also recorded on a strip chart recorder as a backup. Data from this system include wind speed (WS), wind direction (WD), standard deviation of horizontal wind direction (Sigma), and ambient temperature (Temp).

RESPONSIBILITIES

- The Field Service Coordinator is responsible for installing the meteorological station and training field staff to operate the meteorological monitoring station.
- The Auditor is responsible for conducting the semi-annual audits and calibration of the meteorological monitoring station.
- The Program Director is responsible for air monitoring program operations.
- The Field Technician is responsible for field support to the meteorological monitoring station operations, as directed by the Program Director.

EQUIPMENT

The following equipment is needed for the meteorological station calibration and operation:

- Digital Volt-Ohm Meter (DVOM), with certified calibration.

PROCEDURES

This section describes the daily, weekly, and bi-weekly duties of the Field Technician.

Routine Operation and Maintenance

Daily Time Marking of Analog Charts and Data Logger Check

Each day, upon arrival at the meteorological monitoring station, the Field Technician should fill out a Meteorological System Checklist Form and verify the correct time on the data logger.

1. Mark the chart paper with a ballpoint pen or felt-tip marker by making a line across the bottom of the exposed area of the chart paper. Write down the date (month/year/day) and time (24-hour clock, Central Standard Time) and indicate with an arrow that this date and time correspond with the line drawn.

2. Compare the time indicated on the chart paper with the actual time and the data logger time. If they do not coincide, adjust the chart time as necessary.

3. Obtain data logger readings and record on checklist for wind speed and direction.

4. If adjustments were made, remark the chart paper with time and date as before.

Weekly Retrieval/Replacement of Data Cassettes

On a weekly basis, the Field Technicians shall retrieve the cassette tape from the data logger, make a backup tape of the one week of data, and install a new tape to collect data for the next week. All new tapes must be wound past the blank leader, prior to start of data collection.

INSERTING NEW TAPE

Insert a new tape in the recorder. Record the displayed number to determine weekly data's location on the tape. This number will be entered at the next week's visit to copy only the data collected during the week.

Depress the record/play buttons on the recorder. The cassette tape should advance past the blank leader and stop. The system is now on-line for data collection.

REMOVING THE CASSETTE TAPE

The cassette tape should advance, recording all of the residual data in the data logger output buffer. After the data dump, remove the tape.

CASSETTE TAPE COPY

Insert a new tape in the recorder, advance the tape past the blank leader. Change this number to the number recorded during the previous week's visit. Depress the button to dump last week data on the tape as per manufacturer specifications. Remove the tape.

Bi-Weekly Zero/Span Checks (Pre-Checks)

Every two weeks, prior to changing the chart paper, the Field Technician should perform zero/span checks for wind speed (WS), wind direction (WD) and temperature (TEMP), and fill out a Meteorological System Checklist Form. These checks should be done according to manufacturer specifications.

For all parameters checked (WS, WD, TEMP), record the values obtained with the chart reading and the data logger reading on the Zero/Span Check Form, field log book, and the chart paper.

Examples of the checks are as follows:

1. Wind Speed

   a. Set the designated switch in the "Zero" position on the wind speed card. Mark Chart paper as WS zero check and leave the switch in "Zero" position for two minutes. Record data logger reading.

b. Set the designated switch in the "Cal" position on the WS card. Mark chart paper as WS span check and leave the switch in the "Cal" position for two minutes. Record data logger reading.

c. Return the switch to the "Operate" position.

2. Wind Direction

NOTE: Crossarm must be connected for this check.

a. Set the first designated switch in the "Zero" position and the second switch in the "Zero Cal" position on the WD card. Mark the chart paper as WD zero check and leave the two switches in their respective positions for two minutes. Record data logger reading.

b. Set the first designated switch in the "Cal" position and leave the second switch in the "Zero Cal" position on the WD card. Mark chart paper as WD span check (350o) and leave both switches in their respective positions for two minutes. Record data logger reading.

Bi-Weekly Retrieval/Replacement of Chart Paper

The Field Technician should retrieve and replace the chart paper after completion of the bi-weekly zero/span checks as per manufacturer specifications.

Bi-Weekly Zero/Span Calibration Adjustments

If any of the chart readings or data logger readings during the bi-weekly zero/span checks were not within the specifications shown in the calibration log, adjustments should be made per the procedures found in the manufacturer's specifications.

Meteorological System Checklist Form

The meteorological checklist form should be filled out by the Field Technician after completing the daily activities at the meteorological monitoring station. A separate section has to be filled out at the completion of the weekly and bi-weekly activities.

Preventive Maintenance

Preventive maintenance of the meteorological station consists mainly of visual inspection of the individual components for signs of wear or malfunction and performance of the bi-weekly zero/span checks.

Emergency Maintenance

In the event of an equipment failure, the Field Service Coordinator (FSC) should be contacted as to the disposition of the equipment. Emergency maintenance will be based on the use of spare units, as available, with malfunctioning units being sent back to the factory for repair or replacement.

Periodic Calibration

Once every six months, the FSC should conduct a calibration of the meteorological monitoring station, per procedures outlined in the appropriate Sections of this SOP.

RECORDS

Meteorological System Checklist

Meteorological System Checklist Forms should be completed daily for the meteorological station by the Field Technician. The information submitted addresses as-observed equipment conditions and system operation status.

Zero/Span Check Form and Calibration Log Form

The Zero/Span Check Form and Calibration Log Form should be completed by the Field Technician, whenever the bi-weekly zero/span checks or quarterly calibrations are conducted.

Field Log Book

A Field Log Book will be used by the Field Technician to maintain a record of sampling conditions, equipment condition, and calibration data. The information included will be similar to that required for the Meteorological System Checklist Form and Calibration Log Form. The Field Log is considered a backup documentation source and presents information on a chronological basis.

Meteorological Charts

The meteorological charts should be retained by the Program Director. These charts could be used to supplement large periods of missing digital data on an ad hoc basis.

Staff Training Record

Permanent training records should be maintained for the staff relevant to the air monitoring program.

APPENDIX G

DATA VALIDATION CRITERIA AND PROCEDURES

APPENDIX G

DATA VALIDATION CRITERIA AND PROCEDURES

TABLE G-1

SUGGESTED METEOROLOGICAL DATA SCREENING CRITERIA (U.S. EPA, JUNE 1987)

Meteorological Variable	Screening Criteria[a]
Wind Speed	Flag the data if the value: • is less than zero or greater than 25 m/s • does not vary by more than 0.1 m/s for 3 consecutive hours • does not vary by more than 0.5 m/s for 12 consecutive hours
Wind Direction	• is less than zero or greater than 360 degrees • does not vary by more than 1 degree for more than 3 consecutive hours • does not vary by more than 10 degrees for 18 consecutive hours
Temperature	• is greater than the local record high • is less than the local record low (The above limits could be applied on a monthly basis.) • is greater than a 5°C change from the previous hour • does not vary by more than 0.5°C for 12 consecutive hours
Temperature Difference	• is greater than 0.1°C/m during the daytime • is less than -0.1°C/m during the nighttime • is greater than 5.0°C/m or less than -3°C/m
Dew Point Temperature	• is greater than the ambient temperature for the given time period • is greater than a 5°C change for the previous hour • does not vary by more than 0.5°C for 12 consecutive hours • equals the ambient temperature for 12 consecutive hours
Precipitation	• is greater than 25 mm in 1 hour • is greater than 100 mm in 24 hours • is less than 50 mm in 3 months (The above values can be adjusted based on a local climate.)
Pressure	• is greater than 1,060 mb (sea level) • is less than 940 mb (sea level) (The above values should be adjusted for elevations other than sea level.) • changes by more than 6 mb in 3 hours

[a] Some criteria may have to be changed for a given location.

Air Monitoring Data Validation Procedure

Air monitoring data validation efforts should include evaluating collocated station results and audit results to determine data precision and accuracy, as follows:

- The percent difference between the air concentrations measured at collocated samplers is

$$di = \frac{Y_i - X_i}{(Y_i + X_i)/2} \times 100 \qquad \text{(G-1)}$$

Where:

di = The percent difference between the concentration of air toxic constituents Yi measured by the collocated monitoring station and the concentration of air toxics constituent Xi, measured by the monitoring station reporting the air quality.

- The average percent difference dj for the monitoring period is

$$dj = \frac{1}{n} \sum_{i=1}^{n} di \qquad \text{(G-2)}$$

Where:

dj = percent difference defined above.

n = number of samples collected during the monitoring period.

- The standard deviation Sj for the percent differences is:

$$Sj = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^{n} di^2 - \frac{1}{n} \left(\sum_{i=1}^{n} di \right)^2 \right]}$$

- The 95 percent probability limits for precision are:

$$\text{Upper 95 Percent Probability Limit} = dj + 1.96\, Sj \sqrt{2} \qquad \text{(G-4)}$$

$$\text{Lower 95 Percent Probability Limit} = dj - 1.96\, Sj \sqrt{2} \qquad \text{(G-5)}$$

- The accuracy is calculated for the monitoring period by calculating the percent difference dk between the indicated parameter from the audit (concentration, flow rate, etc.) and the known parameter, as follows:

$$dk = \frac{A_k - B_k}{B_k} \times 100 \qquad \text{(G-1)}$$

Where:

A_k = monitor's indicated parameter from the kth audit check.

B_k = known parameter used for the kth audit check.

These results should be compared with the QA/QC criteria stipulated in the monitoring plan to determine data validity.

Other Related Documents

CMA, as part of its ongoing technical education and communication efforts, developed this document as part of its "Chemicals in the Community:" series. Other documents in this and related series include:

CHEMICALS IN THE COMMUNITY Series includes:

Methods to Evaluate Airborne Chemical Levels, May 1988.
A resource document presents two general approaches for placing emission levels in context: data-base driven and model driven. Using these two approaches, 8 methods, are described to evaluate the health impact of airborne releases.

Member price $8.00; Non-member price $12.00.

Implementing Regional Air Monitoring Programs, February 1990.
A manual to assist companies establish regional air monitoring programs. This document covers both the policy issues and the technical details of setting up a regional air monitoring project.

Member price $20.00; Non-member price $40.00.

Understanding Environmental Fate, in preparation.

IMPROVING AIR QUALITY Series includes:

Guidance for Estimating Fugitive Emissions from Equipment, January 1989.
A guidance manual of fugitive emission testing for plants that want to conduct accurate leak rate estimations. This manual includes the EPA protocol with notations for implementation by the chemical industry.

Member price $20.00; Non-member price $30.00.

Fugitive Emission Workshop Videotapes
These videotapes cover some of the topics plant personnel ask about when setting up a testing program for equipment leak, detection, and repair (LDAR).

	Minutes	Member Price	Non-Member Price
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POSSEE Software (Plant Organizational Software System for Emissions from Equipment)
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Member price $150.00; Non-member price $225.00.

A Guide to Estimate Secondary Emissions, In Publication.
A guidance manual for estimation emissions from secondary air sources for SARA 313 reporting.

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				¾ "_____	_____
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				¾ "_____	_____
A Guide to Estimate Secondary Emissions, in Publication		40.00	60.00	_____	_____
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